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# Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: A review

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ABSTRACT

Biomass gasification presents highly interesting possibilities for expanding the utilization of biomass as power generation using internal combustion engines or turbines. However, the need to reduce the tar in the producer gas is very important. The successful application of producer gas depends not only on the quantity of tar, but also on its properties and compositions, which is associated with the dew-point of tar components. Class 5, 4, and 2 tar become a major cause of condensation which can foul the engines and turbines. Hence, the selectivity of tar treatment method to remove or convert class 5, 4, and 2 tar is a challenge in producer gas utilization. This review was conducted to present the recent studies in tar treatment from biomass gasification. The new technologies with their strengths and the weaknesses in term of tar reduction are discussed.



**Contents**



## 1. Introduction

Global climate change due to $CO_2$ emissions is currently debated around the world. This issue has become a major concern and has encouraged the researchers to look for greener sources of energy as alternatives to replace the fossil fuels. Therefore, research activities on renewable energy sources has become more and more important. One of the renewable energy sources is biomass.

Biomass can be converted into energy via thermo-chemical processes such as gasification, direct combustion, and pyrolysis. Among them, biomass gasification presents highly interesting possibilities for expanding the utilization of biomass. Biomass gasification is a thermal conversion process where solid fuel is converted into a combustible gas (producer gas) using gasifying agent

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**Table 1**
Composition of major gas products from biomass gasification [3].

| Gasifying agent | Temperature range (°C) | Gas product (vol.%) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $H_2$ | CO | $CO_2$ | $CH_4$ | $C_{2's}$ | $N_2$ | $H_2O$ |
| Air | 780–830 | 5–16 | 10–22 | 9–19 | 2–6 | 0–3 | 42–62 | 11–34 |
| Steam | 750–780 | 38–56 | 17–32 | 13–17 | 7–12 | 2 | 0 | 52–60 |
| Steam + $O_2$ | 785–830 | 14–32 | 43–52 | 14–36 | 6–8 | 3–4 | 0 | 38–61 |

such as air, steam, etc. It occurs in three stages and begins with drying where inherent moisture in the biomass is removed, then pyrolysis where volatile gases are released, and finally gasification where partial oxidation of residues and volatiles occur. Composition of producer gas from biomass gasification in an atmospheric bubbling fluidized bed gasifier as a function of gasifying agent is shown in Table 1.

Producer gas from biomass gasification can be utilized in internal combustion engines or turbines as power generation, especially in remote areas with no electricity supply. A successful demonstration of a high pressure, low heating value (LHV) gas, biomass integrated gasification and combined cycle (IGCC) was completed in 2000 in the city of Varnarmo, Sweden. This facility is fueled with about 18 MWth equivalent of wood residues and produces about 6 MW of electricity (4 MWe from the gas turbine and 2 MWe from the steam cycle) and 9 MW of heat. The producer gas has a low heating value of about 5–6 MJ/N $m^3$ [1]. Lim and Zainal [2] reported that bubbling fluidized bed gasifiers (BFBG) has potential for rural electrification projects especially in third world countries where biomass supplies are abundant from agricultural industries and where electricity supply from the grid is not available. For rural electrification projects, the bioenergy system is able to supply 100 kWe through a diesel generator, enough for electricity consumption of 50 households.

As the most promising biomass utilization method, gasification produces not only useful fuel gases, char and chemicals, but also some unwanted byproducts like fly ash, $NO_x$, $SO_2$ and tar. Generally, byproducts can cause erosion and corrosion on metals. Belgiorno et al. [4] reported the types of contaminants contained in the producer gas and the potential problems that can be generated as shown in Table 2.

Based on the above description, it is clear that the producer gas from biomass gasification, although providing benefits as an alternative fuel to replace fossil fuel but also has serious problems caused by the byproducts. Tar as one of the contaminants in the producer gas is the main concern of many researchers. Up to now, a great amount of work on tar removal or reduction have been reported. Definition and classification of tar are also reviewed to clearly highlight the condensation, composition, and quantity of tar and the downstream application to which the definition of tar is being applied.

## 2. Tar definition, classification and treatment

Until now, many definitions of tar have been reported. It is usually influenced by the gas quality specifications required for a particular end-use application and how the tar is collected and analysed. One of the definition of tar was reported by Milne et al. [5] as follows: The organics produced under thermal or partial-oxidation regimes (gasification) of any organic material are called "tar" and are generally assumed to be largely aromatic. However, newly contemplated applications of producer gas, such as fuel cells, may be affected by "non-condensables" such as ethylene, cyclopentadiene, and benzene. Other authors describe tar as a complex mixture of condensable hydrocarbons, which includes single to multiple ring aromatic compounds along with other oxygen containing hydrocarbons and complex polycyclic aromatic hydrocarbons [6]. While in the meeting of the IEA Bioenergy Gasification Task, the Directorate General for Energy of the European Commission (DG XVII) and US DoE has decided to define tar as hydrocarbons with molecular weight higher than benzene [7].

Different classifications for tar are found in several literatures [5,6,8]. Milne et al. [5] classified tar into four product classes: (1) primary products which are characterized by cellulose-derived, hemicellulose-derived and lignin-derived products; (2) secondary products which are characterized by phenolics and olefins; (3) alkyl tertiary products which are mainly methyl derivatives of aromatic compounds; and (4) condensed tertiary products which are PAH series without substituent. Primary products are destroyed before the tertiary products appear. Tertiary aromatics can be formed from cellulose and lignin, although higher molecular weight aromatics were formed faster from the lignin-derived products [5].

On the other hand, tar components can be classified into five classes based on their chemical, solubility and condensability of different tar compounds, rather than reactivity of the compounds, as given in Table 3 [6,8,9]. This classification system has been developed by Energy research Center of The Netherlands (ECN), Toegepast Natuurwetenschappelijk Onderzoek (TNO) and University of Twente (UT) in the framework of the project 'Primary measures for the reduction of tar production in fluidized-bed gasifiers', funded by the Dutch Agency for Research in Sustainable Energy (SDE) [9].

**Table 2**
Contaminant presence in the gas and relative problems [4].

| Contaminant | Presence | Problems |
|---|---|---|
| Particulates | Derive from ash, char, condensing compounds and bed material for the fluidized bed reactor | Cause erosion of metallic components and environmental pollution |
| Alkali metals | Alkali metals compounds, specially sodium and potassium, exist in vapour phase | Alkali metals cause high-temperature corrosion of metal, because of the stripping off of their protective oxide layer |
| Fuel-bound nitrogen | Cause potential emissions problems by forming $NO_x$ during combustion | $NO_x$ pollution |
| Sulfur and chlorine | Usually sulfur and chlorine contents of biomass and waste are not considered to be a problem | Could cause dangerous pollutants and acid corrosion of metals |
| Tar | It is bituminous oil constituted by a complex mixture of oxygenated hydrocarbons existing in vapour phase in the producer gas, it is difficult to remove by simple condensation | Clog filters and valves and produce metallic corrosion |

**Table 3**
List of tar compounds that are considered for different tar classes [6,8,9].

| Tar class | Class name | Property | Representative compounds |
|---|---|---|---|
| 1 | GC-undetectable | Very heavy tars, cannot be detected by GC | Determined by subtracting the GC-detectable tar fraction from the total gravimetric tar |
| 2 | Heterocyclic | Tars containing hetero atoms; highly water soluble compounds | Pyridine, phenol, cresols, quinoline, isoquinoline, dibenzophenol |
| 3 | Light aromatic (1 ring) | Usually light hydrocarbons with single ring; do not pose a problem regarding condensability and solubility | Toluene, ethylbenzene, xylenes, styrene |
| 4 | Light PAH compounds (2–3 rings) | 2 and 3 rings compounds; condense at low temperature even at very low concentration | Indene, naphthalene, methylnaphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene |
| 5 | Heavy PAH compounds (4–7 rings) | Larger than 3-ring, these components condense at high-temperatures at low concentrations | Fluoranthene, pyrene, chrysene, perylene, coronene |

Generally, tar content in producer gas depends on the types of gasifier. Tar content from an air-blown circulating fluidized bed (CFB) biomass gasifier is about 10 g/m$^3$. For other types of gasifier, tar content varied from about 0.5 to 100 g/m$^3$ [10]. Tar is the major problem that has not been completely solved so far related to utilization of producer gas in downstream applications. The producer gas will require compression before used in gas turbines and internal combustion engines (ICE) using turbocharger, as well as the air if the gasifier operates at atmospheric pressure. It becomes saturated when the tar vapour pressure exceeds the saturation pressure of the tar and leads to condensation of the saturated vapour. Upon condensation, tar block downstream pipelines and foul engines and turbines.

Several researchers stated that internal combustion gas engines are more tolerant of contaminants than gas turbines. In particular, it is possible to have tar content up to 50–100 mg/Nm$^3$ for ICE and less than 5 mg/N m$^3$ for gas turbines [5]. Typical values of the main components as well as the particulate and tar contents in the raw producer gas from fixed and fluidized bed gasifiers are tabulated as shown in Table 4 [11].

In the case of tar, this problem is fundamentally not concerned with the quantity, but rather the properties and the composition of the tar [12]. The properties and composition of tar are related with the condensation behaviour and component of tar, respectively. Bergman et al. [12] stated that the tar dew-point is a powerful parameter to evaluate the performance of gas cleaning systems. It is believed that, when the dew-point of tar is reduced to levels below the lowest expected temperature, fouling related problems by condensation or tar aerosols are solved. From the relation between the tar dew-point and tar concentration as shown in Fig. 1, class 5 tar dominate the dew-point of tar. Even for very low concentrations of class 5 tar (e.g. <1 mg/m$^3$) dew-point below 100 °C cannot be obtained. The graph clearly points out that, dependent on the concentration in the syngas, classes 2 and 4 need to be partially removed for a proper tar dew-point of about 25 °C. The class 3 tar plays an unimportant role in this matter. Hence, the selectivity performance of tar treatment especially for classes 2, 4, and 5 tar either removed or converted is a key issue for a successful application of producer gas.

The tar removal methods can be categorized in two types, depending on the location where tar is removed; either in the gasifier itself (known as primary method) or outside the gasifier (known as secondary method) [10]. Secondary methods are suitable for tar treatment from producer gas. Two approaches usually used in this method are wet gas and hot gas treatment. Bergman et al. [12] stated that although measures inside the gasifier (primary methods) may be fundamentally more ideal, they have not yet resulted in satisfactorily solutions. Some of the primary measures do result in low tar emissions, but suffer from disadvantages related to, for instance, limits in feedstock flexibility and scale-up, the production of waste streams, a decrease in cold gas efficiency, complex gasifier constructions, and/or a narrow operating window. Although primary measures can reduce the tar content considerably, it is foreseen that complete removal is not feasible without applying secondary measures (see Fig. 2). They also mentioned that a secondary measure can be feasible without needing primary measures. This becomes even stronger when the problems with wastewater treatment can be eliminated as well. A secondary measure should therefore form the basis for tar removal from biosyngas and primary measures could possibly be used for its optimization.

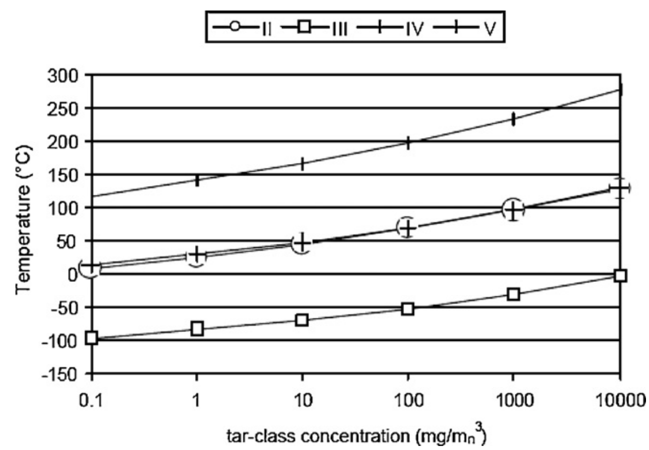



**Fig. 1.** The tar dew-point of the different tar classes in relation to the concentration.

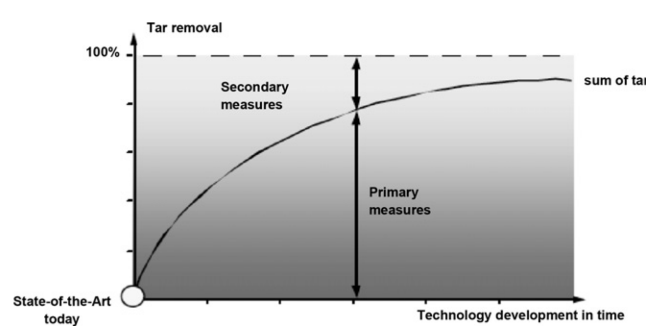



**Fig. 2.** Illustration of the need of primary and secondary measures versus technology development in time [12].

**Table 4**
Gas quality requirements for power generators [11].

| | Unit | IC engine | Gas turbine |
|---|---|---|---|
| Particles | mg/N m$^3$ | <50 | <30 |
| Particle size | μm | <10 | <5 |
| Tar | mg/N m$^3$ | <100 | <5 |
| Alkali metals | mg/N m$^3$ | – | 0.24 |

**Table 5**
Classification of mechanical/physical gas cleaning systems.

| Basic type | Equipment |
|---|---|
| Dry | Cyclone, rotating particle separators (RPS), electrostatic precipitators (ESP), bag filters, baffle filters, ceramic filters, fabric/tube filters, sand bed filters, adsorbers, etc. |
| Wet | Spray towers, packed column scrubber (wash tower), impingement scrubbers, venturi scrubbers, wet electrostatic precipitators, OLGA, wet cyclones, etc. |

## 3. Mechanical/physical methods

Various mechanical/physical gas cleanup systems exist for removal of both particulates and tar from gases produced by biomass gasification. Often these overlap, particularly when tar is present as liquid droplets. Based on application, mechanical/physical methods are divided into two categories: dry and wet gas cleaning. Dry gas cleaning is usually used prior to gas cooling where the temperature is greater than 500 °C and partly below 200 °C after gas cooling, while wet gas cleaning is used after the gas cooling and typically about 20–60 °C. Typical equipment of the dry and wet gas cleaning systems are given in Table 5.

The main use of these devices is to capture particles from the producer gas. The general behaviour for particle collection of mechanical/physical gas cleaning systems is shown in Fig. 3 [14]. This figure shows typical separation efficiency at various particle and droplet sizes based on the type of collection mechanism. A great amount of experimental results demonstrated that the methods are also considerably efficient in removing tar accompanied by effective particles capture. Although tar is often present as vapor, it is removed from the gas as liquid droplets following condensation. Baker et al. [13] mentioned that tar may be present in two forms, in a fixed bed updraft gasifier where the gas exit temperature is low, tar will be present primarily as liquid droplets entrained in the gas. In downdraft and fluidized bed gasifiers where the producer gas is hot, tar may is present in vapor form. Only at high temperatures can particulate and tar removal be separated. At temperatures where tar and oil condense into liquids, removal of tar and oil cannot be divorced from the particulate removal.

### 3.1. Dry gas cleaning

Various dry gas cleaning devices are shown in Table 5. For tar removal cases, cyclone, rotating particle separators (RPS), fabric filters, ceramic filters, activated carbon based adsorbers, and sand bed filters can be used to capture tar from producer gas. However, very few literatures provide information about performance of these devices for tar removal especially from biomass gasification.

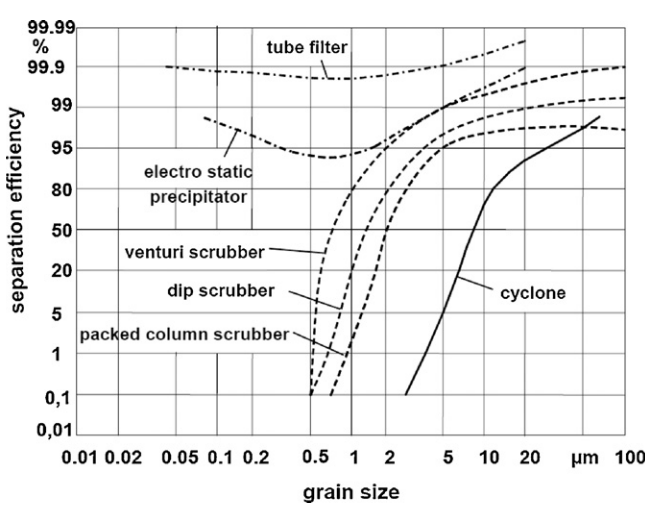



**Fig. 3.** Typical separation efficiencies of mechanical/physical gas cleaning systems.

Based on the preceding concern, no data on efficiency was found on using centrifugal devices for biomass tar removal but for coal gasification, the efficiency of a humidifier/cyclone combination to remove the coal tar is about 50–90% from a pressurized 1 ton/day fixed bed updraft coal gasifier [13]. For RPS and fabric filters, it was reported that 30–70% and 0–50% of tar can be removed, respectively [11]. The author mentioned that fabric filters or the RPS alone will not be able to reduce the tar significantly, and additional tar reduction may be necessary. Similar result was also cited by Rabou et al. [15] in which the RPS can decrease the tar content from 8 to 4.5 g/N $m^3$. The concept of the RPS uses a rotating cylinder which is centered in a single cyclone. This device is more applicable for solid particulates than tar removal [11,16,17].

The excellent gas cleaning by hot gas ceramic filtration was studied by de Jong et al. [18]. Two kinds of ceramic filter were used in this experiment, quartz and glass fibre filter. About 77–97.9% and 75.6–94% tar reduction were achieved from glass and quartz filters, respectively. Nevertheless, ceramic filters have not been considered due to their complexity and high investment. To overcome the weakness of the RPS, fabric and ceramic filters, an additional tar adsorbers based on activated carbon reduction unit is used. Fixed-bed adsorbers such as lignite coke or activated carbon precipitate tar from the producer gas, by means of adsorption of high-boiling tar compounds. Such adsorbers are used for tar separation, waste water processing, etc. of highly contaminated producer gases from biomass gasification plants, such systems are utilized for analytic purposes involving media processing in the laboratory [19].

Hasler and Nussbaumer [11] used activated carbon to remove the tar. Lignite coke has been chosen due to its favorable cost and the good adsorption characteristics. The activated carbon filter is installed at the front of a fabric filter and after the RPS. Tar collection in the range of at least 70% can be expected with additional tar adsorbers based on activated carbon. The use of sand bed filter is also suitable to remove the tar from biomass gasification. It was reported that reduction tar level of 50–97% can be achieved by sand bed filter [11]. Pathak et al. [20] also reported that the percentage reduction in tar and particulate matters is above 90%. Meanwhile, tar deposited in the filter could not be easily cleaned; tar accumulation on the filter surface would lead to eventual plugging. Generally, barrier filters are not suitable for tar removal even though the filters are successfully demonstrated in some cases [41].

The recently developed gas cleaning technique is catalytic filter. This method combines the filtration for particles removal and catalytic cracking of tar from producer gas in one step. A great amount of experimental results demonstrated that the method is also considerably efficient in removing tar and particles [21–24]. It was reported that above 850 °C, a high performance for converting benzene and naphthalene was found using gas velocities typically encountered in candle filtration. The ceramic candle filter contains a nickel-based tar cracking catalyst in the support body [21]. Schematic representation and operation of the catalytic candle filter is shown in Fig. 4. Engelen et al. [23] also revealed that tar removal efficiency between 96% and 98% for naphthalene and 41% and 79% for benzene can be achieved with a co-precipitated catalytic filter disc at a filtration gas velocity of 2.5 cm/s, with 100 ppm of $H_2S$ at a temperature of 900 °C. In the experiments of Ma et al. [25], the conversion of naphthalene is almost complete and a 1000-fold reduction in tar content is obtained with 2.5 wt.% $Al_2O_3$, 1.0 wt.% Ni and 0.5 wt.% MgO porous alumina filter discs at a typical face velocity of 2.5 cm/s, in the presence of $H_2S$ and at 900 °C. The similar result was also obtained with a mixed oxide deposit of 1.20 wt.% $ZrO_2$ + 1.28 wt.% $Al_2O_3$ followed by 0.46 wt.% MgO + 0.996 wt.% Ni [26].

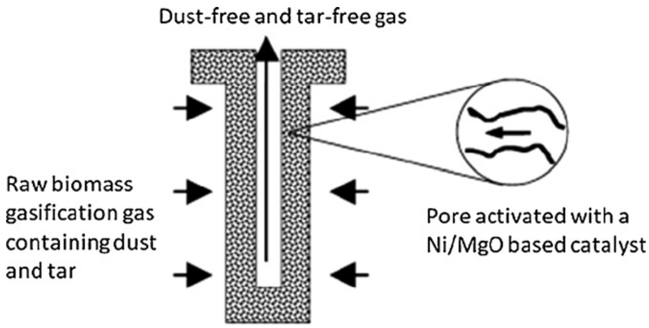



**Fig. 4.** Schematic representation and operation of the catalytic candle filter.

### 3.2. Wet gas cleaning

Wet gas cleaning consists of wet electrostatic precipitators (ESP), wet scrubbers, and wet cyclones as shown in Table 5. These methods have been widely applied in gasification plant (see Table 6). The performance has been approved both in laboratory and industrial scale at various operating parameters. Fig. 5 shows a process flow diagram of a fluidized-bed steam gasification plant with dry dust precipitation and wet gas scrubbing in Gussing, Austria [19] while Fig. 6 shows an integrated biomass gasification and gas cleaning facilities at ECN, Netherlands [27].

A great amount of experimental results demonstrated that the wet gas cleaning is an effective method to remove particles and condensable tar droplets from producer gas. It was reported that the removal efficiency of a wet ESP can reach about 40–70% tar and more than 99% dust in an updraft gasifier at Harboore, a downdraft gasifier at Wiener Neustadt and a circulating fluidized bed gasifier at ECN. A gas residence time of 4 s was enough for total tar removal at voltages between 28 and 34 kV. The cleaned producer gas is able to protect downstream equipment against tar and dust related fouling [28]. The ESP has been also successfully used to clean gas coming out from rotary kiln and saw mill, alkali by-pass, clinker cooler, cement and coal mill [29]. The wet ESP process involves a corona discharge producing ionized gas passing between a high voltage electrode and an earthed (grounded) electrode. The ions attach themselves to the dust particles or droplets of tar and the water when charged are attracted to the grounded electrode due to the electric field. The disadvantages of the ESP is its large size and high capital cost making it suitable for large-scale operations [30].

A wet scrubber forms an important device in wet gas cleaning. The wet scrubber uses water scrubbing to condense the tar from the producer gas and simultaneously removing the particulates. The

**Table 6**
Overview of concepts implemented for gas cleaning and secondary treatment of waste water of various plant concepts [19].

| | Gas cleaning process (GCP) | | | Waste water treatment | Waste water recycling |
|---|---|---|---|---|---|
| | Dry GCP | Wet GCP | Process detail | | |
| Gussing | ☒ | ☒ | Tube filter and wet tar washing | Waste water evaporation | Combustion of residues in the plant |
| Harboore | | ☒ | Quench and wet ESP | Sedimentation waste water evaporation | Combustion of residues in the plant |
| Wiener Neustadt | | ☒ | Quench and wet ESP | Waste water evaporation | Disposal of residues |
| Pyroforce | ☒ | ☒ | Tube filter and wet tar washing | Waste water storage and disposal | Disposal of residues or utilization in the process |
| IWT test facility/shaft gasifier | ☒ | ☒ | Tube filter and wet tar washing | Staged waste water treatment, evaporation, vapor stripping and residue recycling | Recycling in the process, discharge of waste water into the sewer system possible |
| DTU test facility/2-stage gasifier | ☒ | | Dry gas de-dusting with tube filter | Treatment unnecessary | Recycling in the process |
| IWT test facility/multi-stage gasifier | ☒ | | Dry gas de-dusting with tube filter | Treatment unnecessary | Recycling in the process |

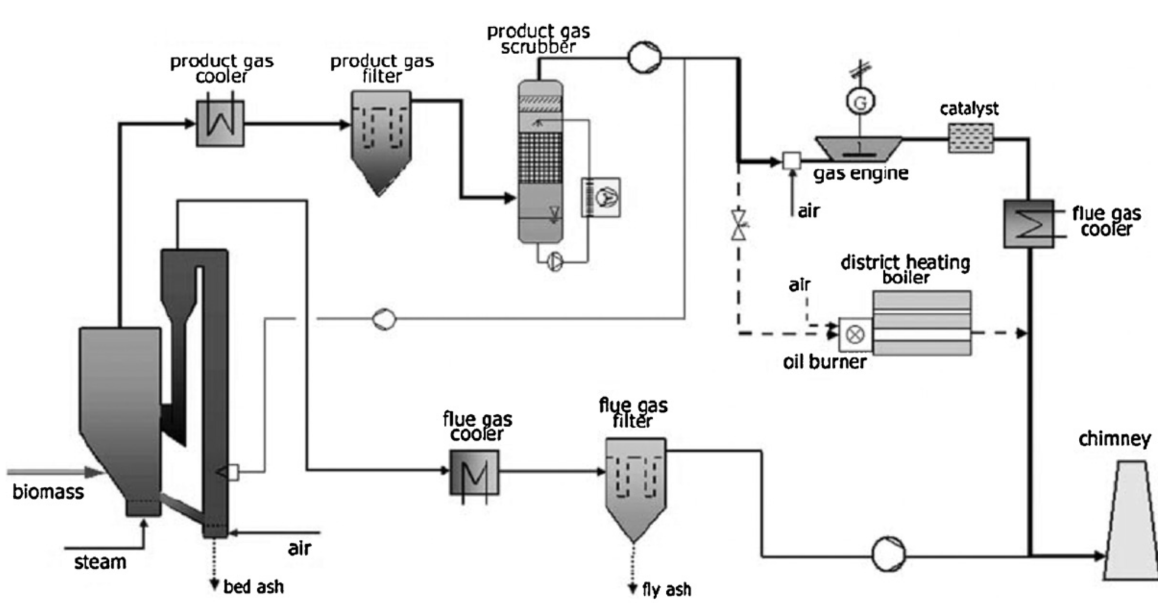



**Fig. 5.** Fluidized-bed steam gasification with dry dust precipitation and wet gas scrubbing in Gussing, Austria [19].

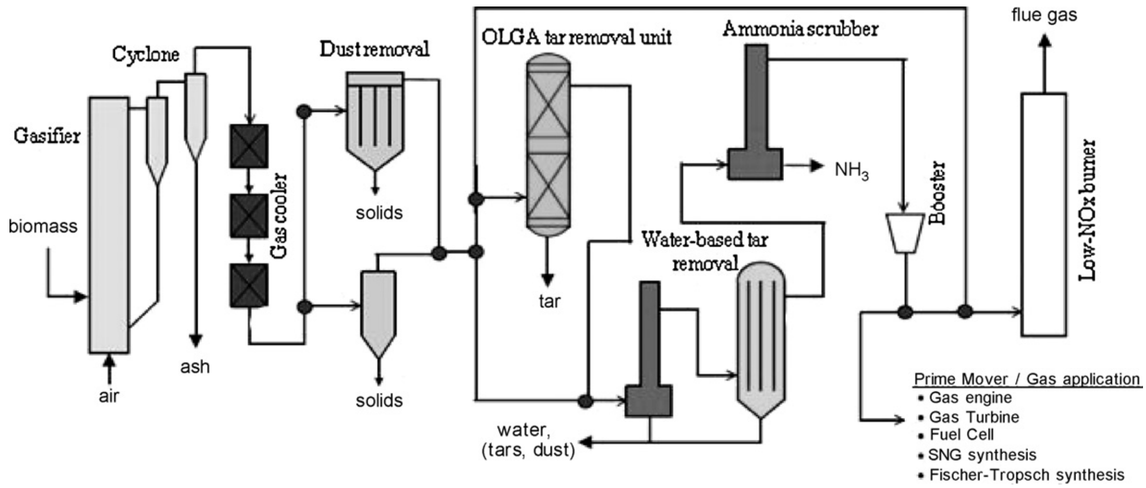



**Fig. 6.** Complete line-up (gas-side) of integrated biomass gasification and gas cleaning facilities at ECN, Netherlands [27].

most common types of wet scrubber are packed column scrubber (spray tower), venturi scrubber, packed bed scrubber, and impingement scrubber (see Figs. 7 and 8). It was reported that tar and particulate levels are reduced to 20–40 mg/m$^3$ and 10–20 mg/m$^3$ in scrubber systems, respectively [31,32]. Spray towers are the simplest, least expensive, and have the lowest efficiency [13].

Bhave et al. [33] investigated a wet packed bed scrubber-based producer gas cooling-cleaning system. The unit will give a clean gas with tar + dust content below the limit of 150 mg/N m$^3$ as long as the inlet gas tar + dust content is below 600 mg/N m$^3$. The system is suited for small scale gasifier-engine system applications and can be scaled up to larger sizes to provide a compact unit. For impingement scrubber, the overall efficiency was about 70%. Higher percentages of tar removal could be achieved by connecting wet impingers in series. Three impingers are needed to obtain efficiencies >95%. Besides being efficient, the wet impinger has the desirable feature of being of simple construction [34].

Venturi scrubber is also highly efficient to remove tar and particle. It was reported that tar separation efficiency ranging from 50% to 90% in a venturi scrubber used to clean the producer gases from a counter-current rice husk gasifier [35]. To optimize the venturi scrubber performance, a simplified 2-D model to predict liquid flux distribution and collection efficiency was studied by Ananthanarayanan and Viswanathan [36]. Showing that the nonuniformity of flux distribution is the key to estimating collection efficiencies accurately. Increase in gas velocity makes flux distribution more uniform and enhances collection efficiencies. An improved algorithm to optimize venturi scrubber performance predicts the minimum pressure drop needed to achieve the desired collection efficiency by optimizing key operating and design parameters such as liquid-to-gas ratio, throat gas velocity, number of nozzles, nozzle diameter, and throat aspect ratio [37].

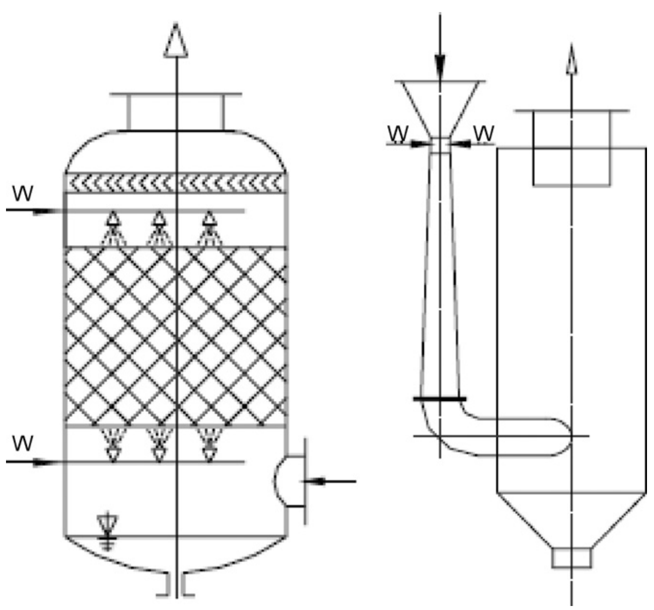



**Fig. 7.** Schematic drawing of: packed column scrubber (left) and venturi scrubber (right) [19].

Generally, wet scrubber uses water to scrub the producer gas. The use of water shows unsatisfactory results with regard to regeneration efficiency and continuous operation behaviour. Crucial disadvantages in using water as a washing medium involve saponification, the low solubility of hydrocarbon compounds, surface tension effects, clogging of apparatus and the comparatively problematical expense of waste water treatment [19]. Lee et al. [38] cited that conventional wet scrubbers also have significant clogging and fouling problems by salt formation at the tip, the inside and outside of the nozzles, the tubes and the walls of scrubbers. Other disadvantages of conventional wet scrubbing systems are the expensive costs for treatment or disposal of the sludge and high operation cost incurred as a result of the improvement of control efficiency. In addition, the heating value of the producer gas and the net energy efficiency of the process become lower after wet cleaning process.

To overcome the disadvantages of wet scrubber, various washing agents are used as scrubber emulsions ranging from pure water up to oil–water mixtures. Scrubber oil emulsions act as solvents, which support the effect of cleaning with regard to tarry compounds and protect the apparatuses themselves from clogging [19]. However, the more serious problem is the high cost of operation. Swirl cyclone-scrubber as shown in Fig. 9 [38,39] has a significantly high and stable particle collection efficiency, negligible pressure drop ranging from 110 to 120 mmH$_2$O, cheap building costs, and low operation and maintenance costs. Also, the system successfully solved the clogging problems inside collection devices by salt formation and/or sticky particulates.

The new gas cleaning system developed at ECN Netherlands is OLGA. A simplified flow sheet of OLGA is provided in Fig. 10. It consists of scrubbing towers interacting with each other in a classical absorption-regeneration mode. Syngas is fed to the tar collector in which tar is removed from the gas to the desired level. The scrubbing liquid with the dissolved tar is regenerated in the stripper.

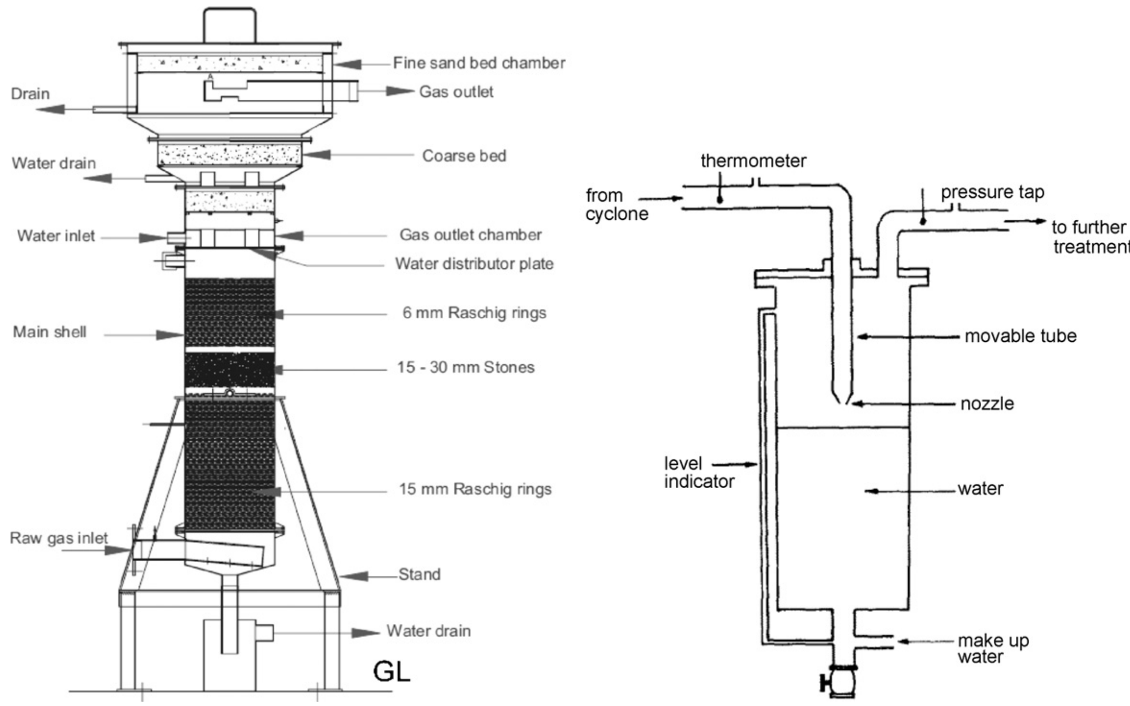



**Fig. 8.** Schematic drawing of: wet packed bed scrubber-based producer gas cooling-cleaning unit (left) [33] and wet impinger (right) [34].

Part of the scrubbing liquid exiting is purged and charged to the gasifier. In case of an air-blown gasification, air is used to strip the tar. Subsequently, the air with the stripped tar is used as gasifying medium [12]. The author stated that despite the high tar collection efficiency of OLGA, no concessions need to be made to other important gasification characteristics, for instance, the cold gas efficiency remains unaffected. Also complex gasifier constructions as a consequence of primary measures are not required. Boerrigter [40] reported that 99% phenol and 97% heterocyclic tar removal can be achieved, which was expected to be high enough to prevent excessive waste water treatment cost due to the pollution of phenol or other water-soluble tar compounds.

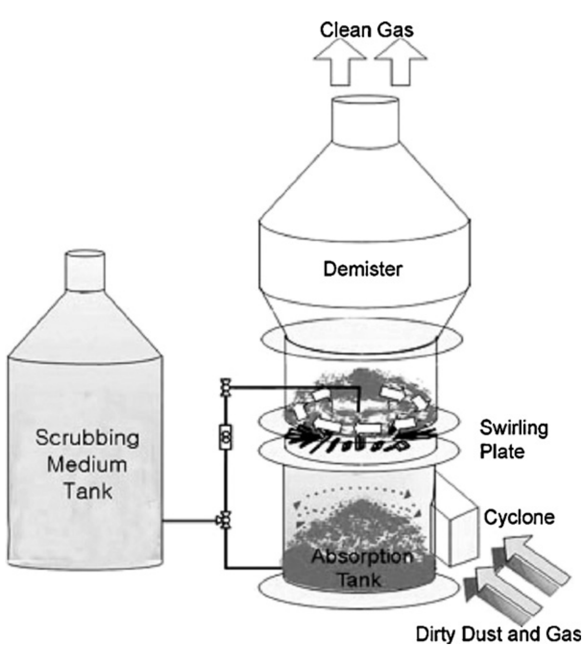



**Fig. 9.** A schematic of the novel swirl cyclone scrubber (NSCS) [39].

A summary of particles and tar reduction from producer gas in various mechanical/physical methods as shown in Table 7 [11].

## 4. Catalytic cracking

There are several types of catalysts that have potential for tar cracking of producer gas [5,10,41–46]. Sutton et al. [42] summarized the criteria for catalyst as follows: (1) the catalysts must be effective in removing tar; (2) if the desired product is syngas, the catalysts must be capable of reforming methane; (3) the catalysts should provide a suitable syngas ratio for the intended process; (4) the catalysts should be resistant to deactivation as a result of carbon fouling and sintering; (5) the catalysts should be easily regenerated; (6) the catalysts should be strong; and (7) the catalysts should be inexpensive.

In application, the potential of catalysts for tar cracking depend on compositions and types of catalysts. Yung et al. [46] reviewed recent investigations of catalyst compositions and their influence on activity for conditioning producer gas. The catalysts composition is divided into three primary components: (1) an active catalytic phase or metal; (2) a promoter, which increases activity and/or stability; and (3) a high surface area support that facilitates dis-

**Table 7**
Reduction of particles and tar in various producer gas cleaning systems (with various definitions of "tar") [11].

| | Temperature (°C) | Particle reduction (%) | Tar reduction (%) |
|---|---|---|---|
| Sand bed filter | 10–20 | 70–99 | 50–97 |
| Wash tower | 50–60 | 60–98 | 10–25 |
| Venturi scrubber | | | 50–90 |
| Rotational atomizer | <100 | 95 ± 99 | |
| Wet electrostatic precipitator | 40–50 | >99 | 0–60 |
| Fabric filter | 130 | 70–95 | 0–50 |
| Rotational particle separator | 130 | 85–90 | 30–70 |
| Fixed bed tar adsorber | 80 | | 50 |
| Catalytic tar cracker | 900 | | >95 |

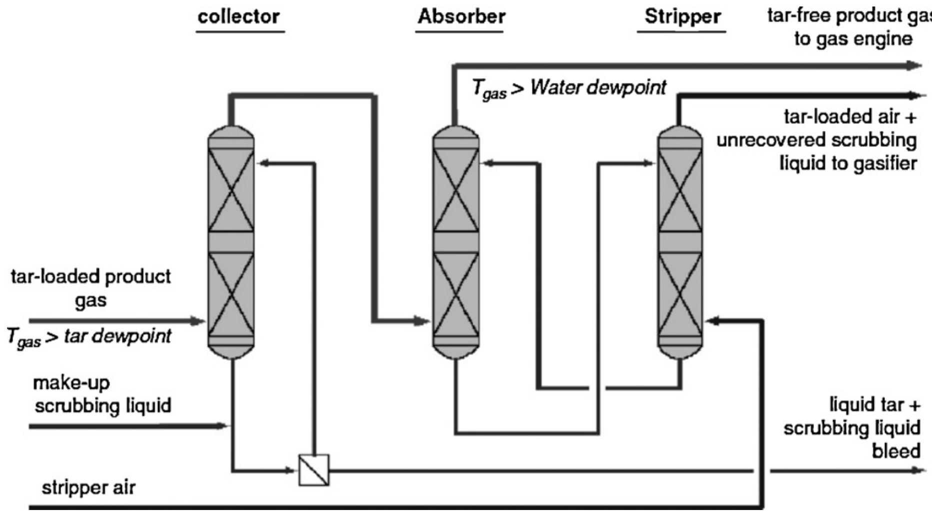



**Fig. 10.** Flow sheet of OLGA.

persion of the active phase. While Han and Kim [41] reviewed tar catalyst cracking and divided into four groups: (1) Ni-based catalysts; (2) alkali metal catalysts; (3) dolomite catalysts; and (4) novel metal catalysts. The catalysts are classified into six groups (nickel-based catalysts, non-nickel metal catalysts, alkali metal catalysts, basic catalysts, acid catalysts, and activated carbon catalysts) and the detailed description are found in the following section.

### 4.1. Nickel-based catalysts

Nickel catalysts of various types have been found to be very effective for tar and as well as for simultaneous ammonia removal in coal or biomass gasification. The use of commercial steam reforming Ni-based catalysts is feasible for tar cracking in biomass gasification. Zhang et al. [47] investigated catalytic destruction of tar in biomass derived producer gas. A tar conversion system consisting of a catalytic reactor was designed to treat the producer gas from an air blown, fluidized bed biomass gasifier. Three commercial steam reforming Ni-based catalysts (ICI46-1, Z409 and RZ409) were proven to be effective in eliminating heavy tar (>99% destruction efficiency). Hydrogen yield was also improved by 6–11 vol% (dry basis). The experimental results also demonstrated that space velocity had little effect on gas compositions, while increasing temperature boosted hydrogen yield and reduced light hydrocarbons ($CH_4$ and $C_2H_4$) formation, which suggested that tar decomposition was controlled by chemical kinetics. Lv et al. [48] used Z409R catalyst for bio-syngas production from biomass catalytic gasification. The author claimed that 83% tar can be cracked at 650–850 °C.

Caballero et al. [49] also investigated three commercial steam reforming Ni-based catalysts (ICI 46-1, BASF G1-50, and Topsoe R-67). They found that the tar cracking efficiency reached 99.8% at 840 °C and gas residence time 0.2–0.3 s. While in the other previous experiments, only about 20–60% and 40–80% tar was cracked using ICI 46-1 and UCI G90-C respectively [50,51]. In the experiment of Corella et al. [52], tar cracking efficiency ranged from 12% to 96% using BASF AG catalyst. The perfomance of BASF AG catalyst is lower than BASF G1-25 S catalyst with efficiency about 88–97% [53]. The other researchers claimed that 98% tar removal is easily obtained with space velocities of 14,000 $h^{-1}$ using eight different commercial Ni-based catalysts, manufactured by BASF AG, ICI-Katalco, UCI, and Haldor Topsoe [54,55]. Similar result of tar reduction was also reported by Rapagna et al. [56] where the tar yield decreased from 0.1 kg/kg of biomass to 0.4 g/kg of biomass at 18,000 $h^{-1}$ and temperature 830 °C. The use of G-90 B5 (Ni-based) catalyst has the desirable feature of total tar removal [57].

The other commercial Ni-based catalysts like G-90 B, G-90 LDP, G-90 EW, C11-NK, G1-25/1, and V 1693 were tested by Pfeifer and Hofbauer [58]. The experiments showed that catalysts for steam reforming of heavy hydrocarbons (naphtha) are very effective in reforming biomass gasification tar. Conversion rates of 98% of tar was easily obtained with space velocities of about 1200 $h^{-1}$ and temperatures of 850–900 °C. No deactivation was observed over a period up to 12 h. In the case of Ni-monolith catalyst, Ising et al. [59] reported that almost total tar conversion could be achieved for residence times higher than 0.3–0.4 s (depending on the type of catalyst) at 900 °C. In continuous tests runs of more than 150 h no deactivation was observed using monolithic Ni-catalysts. Nevertheless, they have some disadvantages such as relatively low performance, high cost and complex technology.

In general, the composition of Ni-based catalysts consists of an active catalyst, promoter, and support as shown in Table 8. The Ni element is the active site of the catalyst. The promoter increases activity and/or stability, while the support gives a high surface area, durability, and coking resistance. Promoters of transition metal-based catalysts with various elements can positively affect catalyst activity, reducibility, regenerability, and coke resistance [48]. While alkaline earth metals promoters such as magnesium [91], and potassium (K), are added to ensure economical operations under severe conditions [92]. Table 8 shows a summary of catalytic conditioning studies using nickel-based catalysts.

Promoters from transition metal-based catalysts such as Mo, W, Zr, Mn, lanthanides such as La and Ce, and Al have been studied by some researchers [67,69–72,80,81,87–90]. Dou et al. [88] studied NiMo catalyst to remove tar components in high temperature fuel gas cleaning. 1-Methylnaphthalene was chosen as a model of the tar components. They found that the NiMo catalyst is the most effective catalyst compared with CaO, $SiO_2$, $Al_2O_3$, and CuMn for tar removal, and very small amount of build up of coke appeared on the catalyst surface. Good activity and anti-coking ability was also found on NiO/olivine doped with 1.0% $CeO_2$ [81]. Sutton et al. [72] also reported that the use of Ni/Al can increased the catalyst activity and the heating value of the gas stream.

The use of support plays an important role in tar conversion of biomass derived producer gas. Various parameter such as acidity, surface area, pore structure, and electronic structure of the support can affect the catalyst activity [46]. Alumina ($Al_2O_3$) is the most commonly used as a support for Ni-based catalysts [25,60–72].

**Table 8**
Catalytic conditioning studies using nickel-based catalysts.

| Catalyst | | | Operating conditions | Tar cracking (%) | Comment | Reference |
|---|---|---|---|---|---|---|
| Active | Promoter | Support | | | | |
| Ni | Mo | | 250–650 °C, 3000 L/h, 1000 mg/m$^3$ 1-MN | ≈100 (550 °C) | Good durability in 168 h at 550 °C<br>Good anti-coking ability<br>Long-term tests are needed to check the feasibility of catalysts at a commercial scale | [87] |
| Ni | Mo | | 250–650 °C, 3000–9000 L/h, 3000 mg/m$^3$ 1-MN | >80 (550 °C) | The 1-MN conversion and coke yield show significant increments at higher temperature and lower space velocity | [88] |
| Ni | Mo | γ-$Al_2O_3$ | 650–950 °C, 1200–2300 L/h | | Benzene selectivity is more significant over NiMo catalyst than over mineral particles but declining with increasing temperature | [67] |
| Ni | | $Al_2O_3$ | 900 °C | ≈100 | Tar conversion of Ni/$Al_2O_3$ > dolomite > activated alumina catalyst > silica-alumina catalyst > silicon carbide<br>The specific surface area of the catalyst did not determine the ability of the catalyst to decompose tar | [60] |
| Ni | | $Al_2O_3$ | 900 °C, 2.0 and 5 MPa | | Toluene conversion is very high<br>Carbon deposition is also rapid | [61] |
| Ni | | $Al_2O_3$ | 700 °C | 93.7 | The Ni/$Al_2O_3$ had a slightly higher reforming activity than dolomite but lower than Rh/$LaCoO_3$/$Al_2O_3$ catalyst | [65] |
| Ni | | $Al_2O_3$ | 600 °C | 77 | The tar destruction capabilities of the custom made nickel based catalysts is lower than commercial catalysts<br>In terms of energy requirements and tar yield, low temperature catalytic steam gasification of biomass appeared to be much more attractive than high temperature reactions | [66] |
| Ni | | $Al_2O_3$ | 730–850 °C | 100 (No $H_2S$) | Ni/Dolomite has an excellent catalytic activity and anti-coking character | [62] |
| | | $SiO_2$ | | 95–99 (100 ppm $H_2S$) | Ni/$Al_2O_3$ and Ni/$SiO_2$ are not stable and eventually deactivate | |
| | | Dolomite | | | | |
| Ni | | $Al_2O_3$ | 600–650 °C, S/C = 0.5 | 80–100 (POT) | Ni/$CeO_2$ showed smaller amount of coke than other catalysts | [63] |
| | | $ZrO_2$ | | 72–100 (SRT) | Tar conversion:<br>Ni/$Al_2O_3$ > Ni/$ZrO_2$ > Ni/$TiO_2$ > Ni/$CeO_2$ > Ni/MgO > no catalyst | |
| | | $TiO_2$ | | | POT is more effective in tar conversion than SRT reaction | |
| | | $CeO_2$ | | | | |
| | | MgO | | | | |
| Ni | | $Ca_{12}Al_{14}O_{33}$ | 550–850 °C, 6000 L/h | 65–100 | Ni/$Ca_{12}Al_{14}O_{33}$ showed excellent sustainability against coke formation due to the free oxygen in the catalysts | [64] |
| | | $Al_2O_3$ | | | Higher $H_2S$-poisoning resistance property compared to the commercial catalysts | |
| | | $CaO_{0.5}$/$MgO_{0.5}$ | | | Reactivation of the sulfide Ni/$Ca_{12}Al_{14}O_{33}$ is difficult to be completely restored | |
| NiO | | γ-$Al_2O_3$ | 700–900 °C | | Temperature played a great role on the gas yield and composition<br>No deactivation during 3 h test at 900 °C | [68] |
| Ni | $CeO_2$ | $Al_2O_3$ | 600 °C, S/C = 0.5 | | Lower yields of coke and tar<br>Coimpregnation method gives the strong interaction between Ni and $CeO_2$. It can play very important role on the steam gasification of biomass<br>Ni/$CeO_2$/$Al_2O_3$ catalysts prepared by the co-impregnation method exhibited higher performance than Ni/$Al_2O_3$ and Ni/$CeO_2$/$Al_2O_3$ prepared by the sequential impregnation method, especially in terms of tar and coke removal | [69,70] |
| Ni | Ce-$ZrO_2$ | γ-$Al_2O_3$ | 850 °C, S/C = 0.44 | 100 | Excellent catalytic activity, stability, and some sulfur tolerance<br>No coke deposition on the catalysts surface during 7 h test period | [71] |
| Ni | MgO | $Al_2O_3$ | 800–900 °C | 77–100 | The naphthalene conversions drop moderately when the naphthalene loading is increased, in contrast with the concentration influence in the benzene conversion | [25] |
| Ni | – | $Al_2O_3$ | 800 °C | | Ni/$Al_2O_3$ gave the highest activities and efficient for hydrocarbons removal | [72] |
| | Al | – | | | Ni/Al is the most active catalyst | |
| | | $SiO_2$ | | | All Nickel catalysts increased the heating value of the gas stream | |
| | | $ZrO_2$ | | | | |
| | | $TiO_2$ | | | | |
| Ni | Al | | 700 °C, S/B = 0.49–2.74 | | The increase of the S/B ratio has a positive effect on the life of the catalyst<br>Catalyst deactivation decreases the $H_2$ yield | [89] |

Table 8 (*Continued*)

| Catalyst | | | Operating conditions | Tar cracking (%) | Comment | Reference |
|---|---|---|---|---|---|---|
| Active | Promoter | Support | | | | |
| Ni | $CeO_2$ | $ZrO_2$ | 550–700 °C | 43.2–87.2 | 15 wt.% Ni/$CeO_2$(75%)–$ZrO_2$(25%): the highest catalytic performance | [90] |
| Ni | Mg | | 850–900 °C | 76 | Nickel catalysts led to the highest gas yields and lower $NH_3$ contents (Ni–Mg > Ni–dolomite > C49 TRX > G-72-D > olivine > dolomite)<br>The use of catalysts as the gasification medium might not be the best way since it is more expensive | [91] |
| Ni/NiO | | MgO | 650–850 °C, 15,000 L/h | 75–100 | The NiO–MgO catalyst exhibited excellent reducibility and highly stable activity for the reforming of raw fuel gas without prereduction but relatively low activity below 1023 K<br>No deactivation and very little carbon deposition during 100 h test | [73] |
| Ni | | MgO | 600–800 °C, 1800–14,400 L/h | | Temperature plays an important role for carbon content of reacted catalysts<br>The blockage of carbon deposition on Ni active site limits the efficiency and causes the catalyst deactivation | [74] |
| NiO | | MgO | 750 °C | 67.4–100 | Excellent stability and highly activity since nickel particles are highly dispersed on the catalyst<br>Steam addition increases the catalyst activity and stability and decreases the carbon deposition on the catalyst | [75] |
| Ni | | $MgO_x/CaO_{1-x}$ | 550–850 °C, 6000 L/h | 30–100 | The preparation methods and concentration of MgO has an important influence on toluene conversion and products<br>Excellent activity of tar steam reforming | [76] |
| Ni | | $Ca_{12}Al_{14}O_{33}$<br>$12CaO.7Al_2O_3$<br>$CaO_x/MgO_{1-x}$ | 500–800 °C | 52–100 | Higher toluene reforming activity and long-time durability comparing to commercial catalyst<br>Superior resistance to carbon poisoning | [77] |
| Ni | | Dolomite | 645 °C | ≈100 | Very effective in tar removing, with conversion values close to 100%<br>A newly developed Ni/dolomite combined catalyst and sorbent has a similar toluene conversion with the commercial nickel catalyst but it must be further investigated to verify the catalyst feasibility | [78] |
| Ni | | Dolomite | 750 °C, 12,000 L/h | 97 | Ni/dolomite is very active for tar removal (Ni/dolomite > ICI-46-1 > Z409)<br>No obvious deactivation of catalyst in 60 h test | [79] |
| Ni | $WO_3$<br>– | Dolomite<br>Dolomite | 780 °C | | Ni/dolomite catalyst gave the best performance for tar cracking<br>Ni–$WO_3$/dolomite catalyst resisted sulfur and coking. It is the best catalyst | [80] |
| NiO | $CeO_2$ | Olivine | 700–830 °C, 862 L/h, S/C = 5 | 34.4–70.4 | Good activity and anti-coking ability at 3.0% NiO/olivine doped with 1.0% $CeO_2$<br>Natural olivine showed good performance as a support. The hardness, density and basicity are compatible with the gasification environment<br>The reaction is controlled by chemical equilibrium | [81] |
| Ni | | Olivine | 750–900 °C | | The presence of excess steam appeared to limit coking than that of the limited steam in the naphthalene-steam reforming | [82] |
| Ni | | Olivine | 560–850 °C | 29–100 | MgO enhanced steam adsorption, facilitating the gasification of surface carbon<br>Ni–Fe alloys prevented carbon deposition by dilution effect<br>Carbon deposit is negligible at 800 °C due to the specific Ni–olivine interactions<br>The catalyst has very good stability (no deactivation) during the 30 h test since the presence of NiO–MgO solid solution on the surface of the olivine support and formation of Ni–Fe alloys | [83,84] |
| Ni | | Olivine | 750–900 °C, 1166 L/h | 85–100 | Differences in surface area did not appear responsible for the differences in catalytic activity<br>The types of olivine support affected the catalytic activity and stability | [85] |
| Ni | | Zeolite<br>$SiO_2/Al_2O_3$ | 750 °C, 12,800 L/h | 99.5 | Impregnation of nickel on zeolites improved the activity<br>Nickel-supported ZY-30 and ZY-80 has the best naphthalene conversions and very stable until 97 h test<br>Coke deposition and catalyst surface area affected the catalytic activity | [86] |

Nickel alumina ($Ni/Al_2O_3$) catalyst gave the highest activity and efficiency for tar removal [72] but it is not stable and eventually deactivate [62]. Simell and Bredenberg [60] describes the order of tar conversion activity as $Ni/Al_2O_3$ > dolomite > activated alumina catalyst > silica–alumina catalyst > silicon carbide. The specific surface area of the catalyst does not determine the ability of the catalyst to decompose tar. Similar result also reported by Simell et al. [61]. They investigated the effects of producer gas components on tar and ammonia decomposition over hot gas cleanup catalysts. Tests were carried out in a fixed-bed tube reactor at 900 °C under 2 and 5 MPa pressure with toluene as tar. They found that the presence of toluene increased the ammonia reaction rate on the nickel catalyst ($Ni/Al_2O_3$). Besides, toluene conversion with the nickel catalyst is very high, i.e. the residual amount of toluene and benzene is quite low. However, carbon deposition is also rapid.

In the experiment of Ammendola et al. [65], the $Ni/Al_2O_3$ had a slightly higher reforming activity than dolomite but lower than $Rh/LaCoO_3/Al_2O_3$ catalyst. They found that more than 93% of tar can be converted into gas using $Ni/Al_2O_3$ catalyst. The behaviour of $Ni/Al_2O_3$ catalyst at low temperature catalytic steam gasification of biomass was investigated by Moghtaderi [66]. The reactor temperature, characteristics of catalysts employed, steam content of the feed gas, and residence time had strong effects on the gas and tar yields, as well as, the distributions of gaseous species in the producer gas stream. The most optimum conditions for low temperature catalytic steam gasification of biomass appeared to be at a reactor temperature of 600 °C, a residence time of 20 min, a steam content of 90% and a nickel based catalyst with an NiO molar ratio of 50%. However, the tar destruction capabilities of the custom made nickel based catalysts is lower than commercial catalysts. Modification of $Al_2O_3$ support by combining it with an additive material can improve the catalytic performance. It was reported that the use of $NiO/\gamma\text{-}Al_2O_3$ as a catalyst for steam gasification of municipal solid waste (MSW) revealed better catalytic performance with increasing producer gas yield and decreasing char and liquid yields. The 3 h test exhibited no deactivation at the temperature of 900 °C [68].

Besides additive material, many researchers tested supports other than $Al_2O_3$ to improve the catalyst performance such as $ZrO_2$, $TiO_2$, $CeO_2$, MgO and $SiO_2$ [62,63,72–75,86], mayenite ($Ca_{12}Al_{14}O_{33}$) [64,77], zeolite [86] or natural supports such as dolomite and simulated dolomite ($MgO_x/CaO_{1-x}$, $CaO_x/MgO_{1-x}$), and olivine [62,72,76,78–85]. Activity test of $Ni/Al_2O_3$, $Ni/ZrO_2$, $Ni/TiO_2$, $Ni/CeO_2$ and Ni/MgO catalysts in partial oxidation (POT) and steam reforming of tar (SRT) derived from the pyrolysis of cedar wood was performed by Miyazawa et al. [63]. They found that the order of activity at 873 K to be $Ni/Al_2O_3$ > $Ni/ZrO_2$ > $Ni/TiO_2$ > $Ni/CeO_2$ > Ni/MgO > no catalyst. Regarding the amount of coke, $Ni/CeO_2$ showed lower amount of coke than other catalysts.

Li et al. [64,77] developed a new nickel-based catalyst (Ni/mayenite) for biomass tar steam reforming producing $H_2$-rich syngas. They observed that $Ni/Ca_{12}Al_{14}O_{33}$ showed excellent sustainability against coke formation due to the free oxygen in the catalysts and higher $H_2S$-poisoning resistance property compared to the commercial catalysts. In addition, the $Ni/Ca_{12}Al_{14}O_{33}$ catalyst exhibited higher toluene reforming activity and long-time durability compared to commercial-like catalyst: $Ni/Ca_x/MgO_{1-x}$ and $MgO_x/CaO_{1-x}$.

Zeolites are an important class of crystalline aluminosilicates, which have been widely used in heterogeneous catalysis because of their well-defined pore structures with extremely high surface area and surface acidity [46]. Buchireddy et al. [86] investigated the catalytic activity of nickel supported zeolites for tar removal. They reported that impregnation of nickel on zeolites improved the activity significantly due to the steam reforming ability of nickel. Long-term catalytic activity tests were performed, the results of which showed that nickel-supported ZY-30 and ZY-80 had the best naphthalene conversions (>99%), followed by nickel-supported ZY-5.2, $SiO_2/Al_2O_3$, and chabazite. Also, very little loss in activity over a 97 h test period was noticed for nickel supported ZY-80 and ZY-30.

In term of natural supported catalyst, dolomite and olivine have been widely used for tar conversion in biomass gasification. Felice et al. [78] reported that combination of Ni/dolomite is very effective in tar removing, with conversion almost 100%. Wang et al. [79] obtained a minimum steam-to-carbon (S/C) ratio for Ni/dolomite of 2.5 at 750 °C to prevent the formation of coke. They also mentioned that Ni/dolomite catalyst is cheap and has excellent activity and anticoke ability. Similar with dolomite, olivine also showed good performance as a support. The hardness, density, and basicity are compatible with the gasification environment [81,83,84].

Base on the above description, it can be concluded that the Ni-based catalysts not only have advantages such as their ability to attain complete tar elimination at temperatures of around 900 °C and increase the yields of CO and $H_2$ but also have some weaknesses such as their rapid deactivation from sulfur and high tar contents in the feed and the need for preconditioning of the feed before it enters the catalyst bed [92]. In addition, such catalysts are relatively expensive.

### 4.2. Non-nickel metal catalysts

Non-nickel metal catalysts such as Rh, Ru, Pd, Pt, etc. have been developed to reduce tar from biomass gasification. Several literatures reported that the use of these catalysts are effective to convert tar into fuel gas. In general, although the non-Ni metal catalysts can significantly reduce tar but the catalysts are more expensive than the conventional or nickel catalyst. Catalytic conditioning studies using non-nickel metal catalysts are given in Table 9. Among these catalysts, Rh catalyst has better performance than commercial catalysts [65,93–101]. The order of the gasification performance is as follows: Rh > Pt > Pd > Ni = Ru, and it is concluded that Rh is an effective component [98].

To increase the catalyst activity, Asadullah et al. [93] used $CeO_2$ as a support for cellulose gasification, however, the sintering of $CeO_2$ suddenly deactivated during the reaction. To prevent the sintering of $CeO_2$, they loaded $CeO_2$ on $SiO_2$ to prepare $CeO_2/SiO_2$ where the catalyst exhibited stable performance in the continuous feeding system. The amount of coke deposited is much lower than commercial steam reforming catalyst and almost all the tar can be converted into producer gas at lower temperature with high energy efficiency [94]. In the experiment of Miyazawa et al. [99], the $Rh/CeO_2/SiO_2$ catalyst is more stable than the Ni catalyst. The results indicate that the $Rh/CeO_2/SiO_2$ has high resistance to coke formation, and this is related to higher combustion activity of $Rh/CeO_2/SiO_2$ than the Ni catalyst.

The performance of $Rh/CeO_2/SiO_2$ is very dependent on the loading amount of $CeO_2$ [95,98]. Asadullah et al. [95] reported that 60% $CeO_2$ on $SiO_2$ is the most suitable. Besides, Polychronopoulou et al. [100] found that the use of 0.5 wt.% Rh loading has better catalytic performance in terms of specific (per gram of Rh) integral hydrogen production rate than the use of 1.5 wt.% Rh loading. The types of the feedstock are also affect the performance of $Rh/CeO_2/SiO_2$. For cedar wood gasification, the tar is not formed at all even at 823 K although a small amount of coke is formed on the catalyst surface. However, in the case of other biomass, especially for rice straw, a significant amount of coke on the catalyst surface and tar is formed even at the high temperature (923 K) [97]. Combination of Rh and $LaCoO_3$ also reduces coke deposition through the prevention of less reducible $Rh(AlO_2)_y$ formation and preservation of reforming properties of rhodium oxide [101]. The $Rh/LaCoO_3/Al_2O_3$ was found to completely convert the condensable tar as well as the light hydro-

**Table 9**
Catalytic conditioning studies using non-nickel metal catalysts.

| Catalyst | | | Operating conditions | Tar cracking (%) | Comment | Reference |
|---|---|---|---|---|---|---|
| Active | Promoter | Support | | | | |
| Rh | $CeO_2$ | $SiO_2$ | 550–700 °C | ~100 | The char and coke formation is very low<br>The deactivation problem was not severe in at least 20 experiments<br>The cost of this catalyst is relatively higher than conventional catalyst | [96] |
| Rh | $CeO_2$ | $SiO_2$ | 550–700 °C | | The $Rh/CeO_2$ catalyst is very active for cellulose gasification, however, the sintering of $CeO_2$ suddenly deactivated the catalyst during reaction | [93] |
| | – | $CeO_2$ | | | The amount of char deposition in the order of $Rh/CeO_2/SiO_2 < Rh/CeO_2 <$ G-91 | |
| Rh | $CeO_2$ | $SiO_2$ | 550–700 °C | ~100 | This performance was much higher than that over commercial steam reforming catalyst<br>The amount of coke deposited on $Rh/CeO_2/SiO_2$ is much smaller<br>Almost all the tar can be converted to syngas at lower temperature than that needed by the conventional method with high energy efficiency<br>The powder catalyst is pressed to granules, has a problem as regards the physical strength | [94] |
| Rh | $CeO_2$ | $SiO_2$ | 550–700 °C | ~100 | $Rh/CeO_2/SiO_2$ exhibited higher performance and more stable than the Ni catalyst, especially in terms of tar and coke amount<br>$Rh/CeO_2/SiO_2$ has high resistance to coke formation | [99] |
| Rh | $CeO_2$ | $SiO_2$ | 550–700 °C | | No severe deactivation was observed even in the longer reaction time (4 h) | [94] |
| Rh | $LaCoO_3$ | $Al_2O_3$ | 700 °C | ~100 | The proposed catalyst exhibits much better performances than conventional catalysts<br>It is able to completely convert tar and also to strongly decrease coke formation due to its good redox properties | [65] |
| ZnO (G-72D) | - | $Al(OH)_3$ | 850–900 °C | | The use of G-72D and of C49 TRX did not produce any significant improvement in tar reductions over natural minerals catalysts | [91] |
| $Co_3O_4$ (C 49-TRX) | $Mo_3O$ | $Al_2O_3$ | | | | |
| Rh, Pd, Ir, Pt | | $Al_2O_3$, $SiO_2$, $ZrO_2$, $CeO_2$ | 300–600 °C | | The catalytic performances of Rh and Ir catalysts is hardly affected by a choice of a metal oxide support | [102] |
| Pt, Ru, Pd | Mo | $\gamma$-$Al_2O_3$ | 310 °C, 5 MPa | | The Mo loading and specifically the Pt/Mo ratio, which determine the Pt dispersion, influence the sulfur resistance of the catalyst<br>The naphthalene conversion (%) decreased as follows:<br>CoMo > PtMo(15) > PtMo(2) > RuMo > PdMo | [103] |
| Rh | $CeO_2$ | $SiO_2$ | 550–700 °C | | In the gasification of different biomasses, the product distribution and carbon conversion were much dependent on the characteristics of each type of biomass<br>The carbon and oxygen content in the biomass was in the order of cedar wood > jute stick > bagasse > rice straw | [97] |
| Rh | $CeO_2$ | $SiO_2$ | 550–700 °C | | $Rh/CeO_2/SiO_2$ gave higher yield of syngas than the conventional steam reforming Ni catalyst<br>Single bed reactor was effective in the gasification of cedar, however, it was not suitable for the gasification of rice straw since a rapid deactivation was observed | [98] |
| FeO | | | 700–900 °C | ~100 (900 °C) | The iron oxides did not demonstrate any catalytic activity | [105] |
| $Fe_2O_4$ | | | | | | |
| $Fe_3O_4$ | | | | | | |
| $MoO_3$ | | SiAl | | | Addition of cerium to molybdenum had a favorable effect on the production of light olefins in the TCC of n-hexane up to a certain level of cerium loading | [104] |
| $CeO_2$ | | SiAl | | | In fact, high loadings of molybdenum and/or cerium favored the formation of aromatics, instead | |
| $MoO_3$–$CeO_2$ | | SiAl | | | | |
| $MoO_3$–$CeO_2$ | | – | | | | |
| $Fe(NO_3)_3{\cdot}9H_2O$ | | | 700 °C | | Iron reduces the production of organics<br>The gas content is significantly increased during the pyrolysis | [106] |

Table 9 (*Continued*)

| Catalyst | | | Operating conditions | Tar cracking (%) | Comment | Reference |
|---|---|---|---|---|---|---|
| Active | Promoter | Support | | | | |
| Rh | $LaCoO_3$ | $Al_2O_3$ | 700 °C | | All catalysts completely convert tar into syngas with small quantities of $CH_4$ and $CO_2$<br>More reducible catalysts also strongly improve tar reforming and inhibit coke deposition | [101] |
| $LaNiO_3$ | | | 700 °C | | The catalytic activity decreases with the increase of the $H_2S$ concentration | [107] |
| Rh | | $CeO_2$ | 575–730 °C, 80,000 L/h | | The 1.5 wt.% Rh/Ce–Zr–O catalyst, the support of which was prepared by the sol–gel method, exhibits better performance than a commercial Ni-based catalyst both solids examined under the same experimental conditions | [100] |
| | | $ZrO_2$ | | | Supported-Rh catalyst showed also no more than 18% drop in activity after 24 h of continuous reaction | |
| | | $SiO_2$<br>$CeO_2$–$SiO_2$<br>$ZrO_2$–$SiO_2$<br>$CeO_2$–$ZrO_2$ | | | | |

carbons, thus, being by far more active than the $Ni/Al_2O_3$ catalyst [101].

Besides Rh catalyst, other metal catalysts like Pd, Pt, Ir, Ru, Co, Fe, Zn, Mo, and La have been tested by some researchers, not only for tar reduction but also for NO reduction [91,102–107]. In the case of NO reduction, Okumura et al. [102] investigated the effect of combination of noble metals and metal oxide supports on catalytic reduction of NO. It is also noted that $CeO_2$ and $ZrO_2$ supports are more effective than $Al_2O_3$ and $SiO_2$ supports for Pt and Pd on NO conversion rate and $N_2$ formation selectivity at relatively low temperatures. In the case of tar and nitrogen compounds abatement, Pinto et al. [91] investigated the effect of catalysts on the quality of syngas and by-products obtained by co-gasification of coal and wastes. They reported that the use of G-72D (mainly composed by zinc oxide) and of C49 TRX (contained mainly cobalt and molybdenum oxides) did not produce any significant improvement in tar reductions over natural minerals catalysts. The effect of catalysts on tar destruction and on gas yields were in opposite directions. The catalysts that led to the lower tar contents also produced the highest gas yields. Therefore, nickel catalysts led to the highest gas yields.

Perez-Martinez et al. [103] observed the effects of the $H_2S$ partial pressure on the performance of bimetallic noble-metal molybdenum catalysts in simultaneous hydrogenation and hydrodesulphurization reactions. The results show that the Mo loading and specifically the Pt/Mo ratio, which determine the Pt dispersion, influence the sulfur resistance of the catalyst. The naphthalene conversion (%) decreased as follows: CoMo > PtMo(15) > PtMo(2) > RuMo > PdMo.

Metallic iron as a tar breakdown catalyst was investigated by Nordgreen et al. [105] and Bru et al. [106]. The producer gas has significantly lower tar content than when no catalyst was used but has higher tar content than using dolomite as catalyst [105]. Bru et al. [106] mentioned that these catalysts increase the $H_2$ production and decrease the $CH_4$ yield, leading the way for a possible use in Fisher Tropsch synthesis and fuel cell applications.

### 4.3. Alkali metal catalysts

Many literatures proved that alkali metal catalysts are also effective in reforming tar and improve the quality of producer gas [108–113]. Wang et al. [109] described that $K_2CO_3$ demonstrated a stronger catalysis for decomposition of hemicellulose, cellulose and lignin constituents, leading to the reduced yield of liquid product in conjunction with the increased yields of gaseous and char products because of the promoted secondary reactions of liquid product. The addition of 17.7 wt.% of $K_2CO_3$, none of saccharides, aldehydes and alcohols was formed and the formation of acids, furans and guaiacols was substantially reduced, whereas the yields of alkanes and phenols were increased. The author also reported that potassium led to an increase in the cumulative yields of $H_2$, $CO_2$ and CO at 700 °C. In the experiment of Xie et al. [110], the influences of additives on the pyrolysis procedure of biomass gasification were investigated at 1073 and 1173 K in a fixed-bed reactor. The results demonstrated that alkali metal carbonates (AMC) mainly increased the yields of permanent gases ($H_2$, $CO_2$, etc.) and improved the quality of gaseous product by promoting the decomposition reactions of tar and light hydrocarbon ($C_nH_m$) and the gasification reaction of char. They also mentioned that AMC should be used as the promoter to enhance the steam gasification of carbon/char deposited on the catalyst. Alkali ion-exchanged catalyst such as $Ca(OH)_2$ was also found to promote the decomposition of cellulose and lignin constituents, and the effect of $Ca(OH)_2$ on the yields of liquid and char is opposite to that of $K_2CO_3$. The addition of 22.2 wt.% $Ca(OH)_2$, some groups of liquid product such as acids and aldehydes have completely disappeared and the yields of saccharides, furans and guaiacols were reduced, while the yield of alcohols were remarkably increased in contrast to the result of $K_2CO_3$. On the other hand, the addition of $Ca(OH)_2$ did not significantly change the total yield of producer gas at 700 °C but enhanced the yield of $H_2$. Huang et al. [112] mentioned that the $CO_2$ gasification reactivity of fir char is improved through the addition of metal catalysts, in the order K > Na > Ca > Fe > Mg.

Gasification of wastepaper using molten carbonate catalysts was investigated by Iwaki et al. [114] and Jin et al. [115]. Experimental results demonstrated that the intermixture carbonates exhibit strongly enhancement on catalytic activity than any carbonate salts. The reaction rate depends on the temperature and a rapid heating processes is more favorable. Encinar et al. [116] studied pyrolysis/gasification of agricultural residues by carbon dioxide in the presence of different additives (NaCl, LiCl, KCl, $AlCl_3{\cdot}6H_2O$, ZnCl). The most significant effect observed is the increase of char fraction and decrease of liquid except when KCl is present. Gas phase also decreases in the presence of additives except when $AlCl_3{\cdot}6H_2O$ is used. Keown et al. [117] also investigated the effects of volatile-char interactions on the volatilization of alkali and alkaline earth metallic (AAEM) species during the pyrolysis of biomass. The results indicate that the volatile-char interactions could lead to the additional volatilization of AAEM species, particularly if the volatile-char interactions have resulted in additional char weight losses.

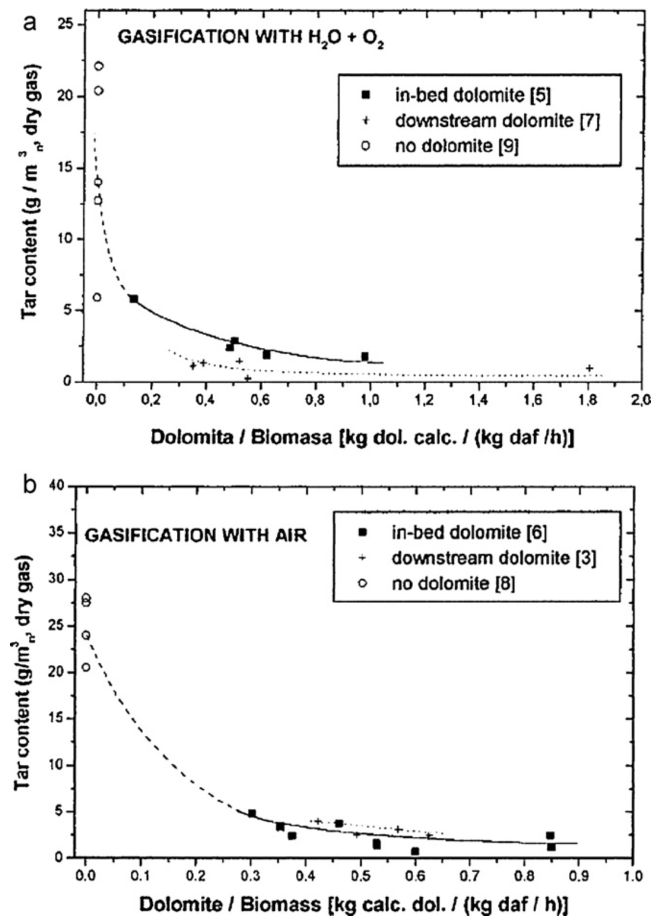



**Fig. 11.** Tar content in the flue gas versus relative amount of dolomite used for two locations of the dolomite and for two gasifying agents; (a) gasification with $H_2O + O_2$ mixtures, gasification ratio (GR) = 0.86 – 1.16, $T$ = 820 – 840 °C; (b) gasification with air, equivalence ratio (ER) = 0.22 – 0.26, $T$ = 800 – 850 °C.

Sutton et al. [42] described that the alkali metal catalysts are often added directly to the biomass by dry mixing or wet impregnation. When added in this way, the catalyst is difficult to recover and this is not always cost effective for the gasification process. It also gives an increase in the ash content after char gasification, and the disposal of this is predicted to become a problem.

### *4.4. Basic catalysts*

Besides the alkali metals, alkaline earth metal oxides (MgO, CaO, etc.), natural ores (dolomite, olivine, etc.) and some clay minerals are also included as basic catalysts. Several studies have been done using these catalysts with considerable reduction of tar in the producer gas [41,42,44,92,110,118]. Increasing the Ca/Mg ratio, decreasing the grain size, and increasing the active metal content such as iron can improve the activity of these catalysts [119]. The Ca improved the formation of crystal structure and Mg enhanced the degree of carbon structure ordering which played a negative role in gasification. On the other hand, Ca metal cannot be used as a catalyst at high temperature, because its particles are inclined to agglomerate, resulting in deactivation [112].

Influence of alkaline earth metal oxides (CaO and MgO) on steam gasification of biomass was studied by Xie et al. [110]. They found that the catalysts mainly increased the yields of permanent gases ($H_2$, $CO_2$, etc.) and improved the quality of gaseous product by promoting the decomposition reactions of tar and light hydrocarbon ($C_nH_m$) and the gasification reaction of char. Norwegian dolomitic magnesium oxide (MgO) showed a higher catalytic decomposing activity on the tar-derived one-ring species toluene than quicklime (CaO) [67]. In the experiment of Siedlecki et al. [120], magnesite showed activity in promoting the water–gas shift reaction, (steam) reforming of methane and $C_2$ hydrocarbons toward their equilibrium, and reducing the tar (toluene, xylenes, polycyclic aromatic hydrocarbons/PAHs, and phenolics). The concentration of PAHs and phenolics is reduced even to 1.9 g/N m$^3$, which is below 2 g/N m$^3$, being considered as an important limit for many downstream applications. However, the activity of CaO and MgO is still below CaO–MgO for tar elimination and gas yield in the following order: calcined dolomite (CaO–MgO) > calcined magnesite (MgO) > calcined calcite (CaO) [121].

The catalytic activity of calcined dolomite was extensively investigated in terms of tar reduction [121–132]. Calcined dolomite catalyst is more active than the un-calcined dolomite for tar decomposition since its large (internal) surface area and oxide contents on the surface. Hu et al. [133] compared a calcined dolomite with an un-calcined dolomite as well as a calcined olivine and raw olivine as downstream catalysts in steam gasification of apricot stone and found that among all the catalysts tested the calcined dolomite is the most effective catalyst for increasing the $H_2$ content in the gas.

The addition of calcined dolomite in the bed material improve the tar conversion [6,123–125], agreed with Corella et al. [134] who stated that the effectiveness of the dolomite in the second reactor is only a little bit higher than for the in-bed location as shown in Fig. 11. This small increase in effectiveness is mainly found in gasification with $H_2O + O_2$ mixtures and there is no chemical differences (between the two locations of the dolomite) in gasification with air. Addition of 17 wt.% (pre-calcined) dolomite converted 90% PAHs and the total tar amount of 4.0 g/N m$^3$ could be reduced to 1.5 g/N m$^3$ [6]. With a 15–30 wt.% of calcined dolomite in the bed, tar contents below 1 g/N m$^3$ can be obtained [123,124]. This in-bed tar elimination causes an increase in the $H_2$ content from 6–10 to 12–17 vol.%, the CO content from 9–16 to 16–22 vol.%, and the $CH_4$ content from 2.5–3.5 to 4.0–5.2 vol.% [123].

Gusta et al. [125] reported that dolomites improved tar conversion to gaseous products by an average of 21% over noncatalytic results at a 750 °C isothermal catalyst bed temperature using 1.6 cm$^3$ dolomite/g of biomass. The iron content in dolomite was found to promote tar conversion and the water–gas shift reaction, but the effectiveness reached a plateau at 0.9 wt.% Fe in Canadian dolomites. The maximum tar conversion of 66% was achieved at 750 °C using a Canadian dolomite with 0.9 wt.% Fe (1.6 cm$^3$/g of biomass) and carbon conversion to gaseous products increased to 97% using 3.2 cm$^3$ dolomite/g of biomass at the same temperature. The dolomite seemed stable after 15 h cyclic use at 800 °C. In the experiment of Wang et al. [79], modified dolomite (mixed of natural dolomite and $Fe_2O_3$ powders) showed higher activity. Tar conversion ranged from 43% to 95% with calcined dolomite catalyst, and 44–97% with modified dolomite.

The effect of dolomite types on tar cracking was also investigated by Yu et al. [126]. They used Chinese dolomites (Zhenjiang, Nanjing, Shanxi, Anhui) and a Swedish dolomite (Sala) in gasification of birch and found that all dolomites except Anhui dolomite effectively decompose tar into gases. Anhui dolomite showed a low catalytic capacity to crack tar produced at 700 and 800 °C and Sala dolomite is more efficient than the Chinese dolomites for cracking naphthalene as shown in Fig. 12. Myren et al. [122] stated that the concentration of naphthalene is of particular interest since it is the most difficult compound to decompose when dolomite is used as catalyst.

Besides dolomite, the activity of olivine catalysts have been also tested for tar conversion by some researchers [6,65,84,91,110,135–138]. Natural olivine works as an excellent tar reduction agent, considerably improving the quality of the gas pro-

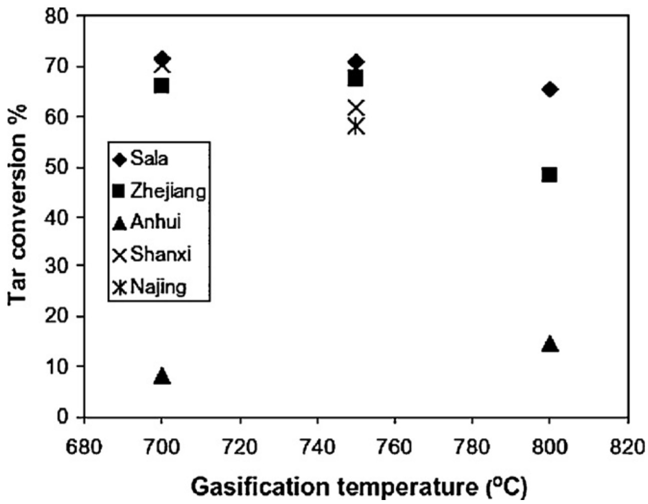



**Fig. 12.** The tar conversion efficiencies (%) of different dolomites plotted versus gasification temperature (°C).

duced, in terms of low tar content, high hydrogen volume fraction, large syngas yield [137] and it does not tend to form coke [65]. Similar results was also described by Xie et al. [110]. Addition of 17 wt.% olivine to the sand during hot gas cleaning leads to a 71% decrease of PAHs at 900 °C and the total tar amount of 4.0 g/N $m^3$ could be reduced to 2.2 g/N $m^3$ [6].

The calcination of olivine improves the catalyst activity as shown in Fig. 13. Devi et al. [135,136] found that the naphthalene conversion of around 30% is observed with 1 h of calcination. With increasing calcination time, tar conversion increases; more than 80% naphthalene conversion is observed with 10 h of calcination time for olivine, which is found to be an optimum. Both steam and dry reforming reaction of naphthalene forms more than 50% gaseous products over 10 h pretreated olivine. Besides the gaseous products and light tar, polymerization reactions occurs producing higher tar in small quantity. Naphthalene conversion under syngas mixture is somewhat lower than that of only in steam and $CO_2$. Kuhn et al. [138] reported that treatments prior to reaction are shown to largely effect the catalytic activity and physiochemical properties of the olivine catalysts depending on its origin. The formation of free Fe phases following decomposition of a Fe-bearing serpentine phase ($(Mg,Fe)_3Si_2O_5(OH)_4$) near the surface of untreated olivine catalysts proved most important for facilitating higher activity compared to olivine catalysts with little or no serpentine phase initially. In their experiment, the naphthalene

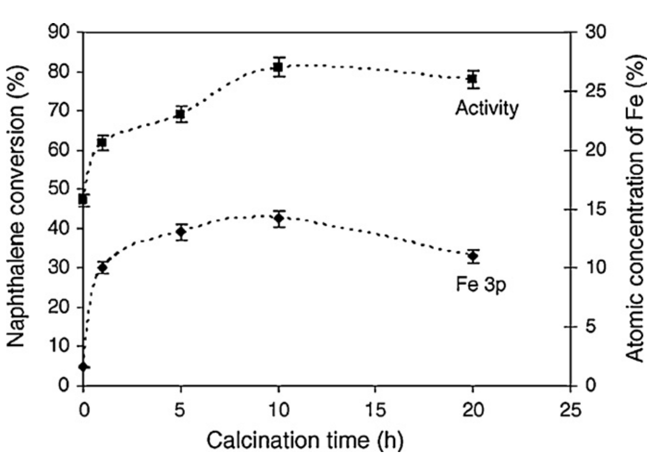



**Fig. 13.** Activity (naphthalene conversion) of olivine and atomic concentration of Fe 3p at the surface of olivine (determined by XPS) as a function of calcinations time.

conversion of around 90% is observed at 800 °C. In contrast, Pinto et al. [91] reported that the lowest hydrocarbons concentrations are obtained in the presence of dolomite, being followed by olivine and afterwards by calcined olivine. Gas yields produced during co-gasification of coal mixed with wastes in the presence of dolomite are higher than those of either natural or calcined olivine.

Although the dolomite and olivine catalysts can decrease tar but the activity are lower than that of metallic catalysts. Compared to nickel, magnesium, zinc, cobalt and molybdenum oxides, dolomite and olivine are less effective in tar destruction. Dolomite and olivine are also the least active to convert light hydrocarbons compared to $Ni/Al_2O_3$ and $Rh/LaCoO_3/Al_2O_3$. Besides, olivine showed much less oxidation, reforming and cracking activity [65]. The accumulation of carbon on the dolomite bed is 6–20 times greater than on the metallic catalysts [47]. Swierczynski et al. [84] described that at 750 °C olivine shown practically no activity (toluene conversion <5%) and moderate activity at 850 °C (only 37%). The olivine has significant selectivity toward heavier polyaromatics (14%), benzene (~6%) and methane (2%) formed additionally to CO, $CO_2$ and $H_2$. Very low quantity of carbon is formed on olivine after tests at 750 and 850 °C.

### *4.5. Acid catalysts*

Zeolite, silica-alumina, etc. are the acid catalysts. Zeolites are crystalline silicates and aluminosilicates linked through oxygen atoms, producing a three-dimensional network containing channels and cavities of molecular dimensions [150]. Zeolites are solid catalysts with the following properties: (1) high surface area, (2) molecular dimensions of the pores, (3) high adsorption capacity, (4) partitioning of reactant/products, (5) possibility of modulating the electronic properties of the active sites, and (6) possibility for preactivating the molecules by strong electric fields and molecular confinement [150]. The acidic properties (Bronsted sites) of zeolites are dependent on the method of preparation, form, temperature of dehydration, and Si/Al ratio. The key properties of zeolites are structure, Si/Al ratio, particle size, and nature of the (exchanged) cation. These primary structure/composition factors influence acidity, thermal stability, and overall catalytic activity [92].

Zeolites have been widely used in heterogeneous catalysis because of their well-defined pore structures and capabilities of extremely high surface area and surface acidity [46] and the most used in industrial applications [44] since its commercial availability [150]. The modification of acidic zeolites with dispersed metals produces catalysts suitable for hydrogenation and ring-breaking reactions of aromatic hydrocarbons such as benzene, toluene, naphthalene, and polycyclic aromatics. The catalysts are have relatively high tolerance for sulfur compounds in the context of clean up of gasification effluents [44].

In the case of tar reduction, various kinds of zeolites especially the commercial catalysts were tested by some researchers [86,87,113,139–141,143–147,151,152]. Olazar et al. [143] investigated the effect of acid catalysts (HZSM-5, HY, HBeta) on scrap tyre pyrolysis under fast heating conditions. They found that HZSM-5 is more efficient for the formation of gases, although it contributes only to decreasing the molecular weight of aromatic $C_{10}$-fraction while HBeta zeolite catalyst has an intermediate behaviour. Reforming pyrolysis volatiles at 723 K using a HZSM-5 zeolite catalyst efficiently increases (from 2 to 20 wt.%) the yield of gases, with a high yield of ethene and propene. The yields of tar increases only slightly compared to thermal pyrolysis, due to steric restrictions in the crystal structure of HZSM-5 zeolite.

Catalytic cracking of tar component (1-MN) from high-temperature fuel gas using five catalysts (Y-zeolite, silica, alumina, lime, NiMo) were tested by Dou et al. [87]. The results showed that Y-zeolite and NiMo catalyst to be most effective catalysts. Over

10 h test period, two catalysts almost removed 100% of 1-MN, and deactivations of two catalysts were not yet observed. With other catalysts, deactivation was rapid. The activity of alumina dropped from nearly 100% of 1-MN conversion initially to less than 80% after 9 h. The silica appears to have much less catalytic activity than other catalysts for cracking 1-MN.

Buchireddy et al. [86] also investigated the catalytic activity of zeolites (ZY, Zβ, ZSM5) for tar removal. The effect of pore size and acidity on tar removal were also tested. They found that ZY has better catalytic activity toward naphthalene conversion compared with Zβ and ZSM5 due to its larger pore size. Further, an increase in the acidity of zeolites increases the activity of the catalyst while decreasing its resistance toward coke formation. ZY-5.2, which is more acidic, has the highest activity toward naphthalene conversion compared with ZY-30 and ZY-80. Nomura et al. [145] mentioned that product distribution derived from hydrocracking of phenanthrene is strongly affected by the pore size of the zeolite.

Stability of the zeolite upon catalyst regeneration can be an issue [150]. As the catalysis run time increases the deactivation of the catalyst becomes apparent, with a loss in the selectivity of the catalysis products [152] and reduced the activity of the catalyst [140]. To overcome this problems, Millini et al. [149] stated that the industrial regeneration procedure is able to avoid removal of framework aluminum and zeolite structure collapse, allowing complete restoration of catalyst performances even after several reaction/regeneration cycles in real conditions.

The advantages of zeolites are related to their acidity, better thermal/hydrothermal stability, better resistance to nitrogen and sulfur compounds, tendency toward low coke formation, and easy regenerability. The other advantages with zeolites are their relatively low-price and the knowledge gained about them from long experience with their use in fluid catalytic cracking (FCC) units. However, the main disadvantage with these catalysts is the rapid deactivation because of coke formation [86,92].

Besides zeolites, silica–alumina catalysts were also studied for tar reduction in biomass gasification. Several literatures showed that the catalysts can reduce tar although their activity is lower than the other catalysts [60,61,65,86,87,142,146]. It was reported that SiC and $SiO_2$ are ineffective, converting 0.46–5.14% of the tar into lighter hydrocarbons [139] while $SiO_2/Al_2O_3$ has the least activity toward naphthalene conversion [86]. The activity of alumina dropped from nearly 100% of 1-MN conversion initially to less than 80% after 9 h [87].

Simell and Bredenberg [60] reported that activated alumina totally decomposed the heterocyclic and phenolic compounds of the tar and reduced the amounts of PAH compounds, benzene and benzene derivatives. The amounts of all groups of tar components are also reduced when using silica–alumina, although not to the same extent as when using alumina. The ability of the tested materials to decompose tar decreased in the following order: commercial nickel catalyst (Ni on $Al_2O_3$) > dolomite > activated alumina > silica–alumina > silicon carbide (inert). Ammendola et al. [65] found that the stabilized alumina is very sensitive to coking. The methane released by the biomass in the range 390–660 °C also remained essentially unconverted by alumina.

The performance of alumina in rapid pyrolysis of biomass was also investigated by Hosokai et al. [148] and found that coke was deposited over the alumina particles with a yield of 10–20%, and it acted as a catalyst to eliminate polyaromatic hydrocarbons as the representative constituents of the heavy tar. Thus the mesoporous alumina played a dual role of eliminating tar and controlling the total yield of char and coke, and would therefore be suitable as the bed material for biomass gasification in two stage gasifier with the bed material being circulated between the biomass pyrolysis/steam reforming zone and the char/coke combustion zone.

**Table 10**
Chemical and physical properties of the treated commercial biomass char by heating up to 850 °C and soaking for 30 min [9].

| Component biomass char | Wt.(%) | Error (%) |
|---|---|---|
| Water | 0.2 | ±0.00 |
| Ash | 9.55 | ±0.09 |
| Volatiles | 2.01 | ±0.06 |
| Fixed carbon | 88.24 | (balance) |
| C | 89.03 | ±0.13 |
| N | 0.24 | ±0.01 |
| H | 0.12 | ±0.01 |
| S | <0.01 | |
| C | l 0.02 | ±0.00 |
| Br | <0.01 | |
| F | 0.40 | ±0.05 |
| O | 10 | (balance) |

| Component ash | Wt.(%) | Error (%) |
|---|---|---|
| Na | 1.09 | ±0.01 |
| K | 0.48 | ±0.01 |
| Mg | 12.4 | ±0.1 |
| Ca | 29.9 | ±0.5 |
| Al | 2.21 | ±0.08 |
| Ti | 0.81 | ±0.00 |
| Fe | 9.10 | ±0.01 |
| Si | 0.66 | ±0.02 |
| C | 0.17 | ±0.02 |

| Physical properties | Value |
|---|---|
| BET-surface area | 353 $m^2/g$ |
| Total pore volume | 0.19 $cm^3/g$ |
| Adsorption average pore width (4 V/A by BET) | 29 Å |

### 4.6. Activated carbon catalysts

Activated carbon is widely utilized for adsorption of volatile organic compounds (VOCs), $NH_3$ decomposition and some specific contaminants from gas/liquid streams. Due to their highly porous textural structures, activated carbons or chars (derived from biomass or coal) have also been widely used as catalyst supports for conversions of hydrocarbons and tar cracking, not only because of their macropores and mesopores that would greatly improve the dispersion of metal ions, but also facilitate transport of reactant molecules into the internal surfaces of the catalyst [118]. El-Rub [9] stated that the char catalytic activity for tar reduction can be related to the pore size, surface area, and ash or mineral content of the char as shown in Table 10. The first two factors are dependent on the char production method, such as the heating rate and pyrolysis temperature. The last factor depends mainly on the char precursor type.

The performance of char catalysts for tar conversion are found in several literatures [9,117,127,153–159]. The presence of char is helpful in reducing the amount of tar [153] and aromatics [154]. The reactivity of char may significantly increased by using high heating rates, small particle size of the fuel and short residence time at higher temperature [155]. Besides, char types also influenced the char reactivity. Chars from olive waste and straw are more reactive in gasification than chars from birch because of the higher ash content [156]. Di Blasi et al. [160] also reported that olive husks and straw chars are the most reactive, at slow and fast heating rates, respectively compared to grape residues and pine wood. The reactivity first attains a maximum, decreases or remains almost constant and then increases again as a function of conversion. This behaviour can be explained by the different roles played by the reaction temperature, the development of surface area as combustion proceeds and the increase in the ratio of ash to carbon. While the use of activated carbon (from Ajinomoto Fine Techno Co., Inc.), wood chip (from Japanese cedar, dried in a controlled oven at 105 °C

**Table 11**
Individual light tar compounds and benzene (in mg/g dry raw material) from birch, miscanthus and straw after thermal cracking at 700, 850 and 900 °C [122].

| | Feedstock | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Birch | | | Miscanthus | | | Straw | | |
| | 700 °C | 850 °C | 900 °C | 700 °C | 850 °C | 900 °C | 700 °C | 850 °C | 900 °C |
| Benzene | 0.6 | 1.1 | 2.4 | 3.3 | 3.1 | 5.4 | 0.7 | 0.8 | 0.9 |
| Toluene | 1.5 | 1.5 | 1.7 | 3.2 | 2.7 | 2.2 | 1.1 | 1.1 | 0.7 |
| *p*-Xylene | 0.6 | 0.4 | 0.1 | 0.6 | 0.4 | 0.2 | 0.4 | 0.2 | 0.1 |
| *o*-Xylene | 1.2 | 1.2 | 0.7 | 1.5 | 1.2 | 0.7 | 1.3 | 1.0 | 0.6 |
| Indene | 0 | 0.1 | 0 | 1.3 | 1.4 | 0.6 | 0.2 | 1.0 | 0.4 |
| Naphthalene | 1.0 | 2.5 | 2.3 | 1.6 | 3.3 | 3.7 | 2.2 | 3.3 | 3.9 |
| 2-Methylnaphthalene | 0.1 | 0 | 0 | 0.5 | 0.5 | 0.3 | 0.3 | 0.3 | 0.1 |
| 1-Methylnaphthalene | 0.1 | 0 | 0 | 0.1 | 0.2 | 0.1 | 0.3 | 0.2 | 0.1 |
| Biphenyl | 0 | 0 | 0 | 0 | 0.1 | 0.1 | 0.2 | 0.2 | 0.1 |
| Acenaphthylene | 0 | 0 | 0 | 0.4 | 0.8 | 0.6 | 0.5 | 0.5 | 0.5 |
| Fluorene | 0.1 | 0 | 0 | 0 | 0 | 0 | 0.1 | 0.2 | 0.2 |
| Phenanthrene | 0 | 0 | 0 | 0.2 | 0.5 | 0.5 | 0.3 | 0.3 | 0.6 |
| Anthracene | 0 | 0.3 | 0.3 | 0.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.2 |
| Fluoranthene | 0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 |
| Pyrene | 0 | 0 | 0 | 0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.3 |
| Total light aromatics excluding benzene | 4.6 | 6.1 | 5.2 | 9.6 | 11.5 | 9.4 | 7.2 | 8.6 | 8.0 |

overnight) and synthetic porous cordierite (from Chemical Auto Co., Ltd.) for tar removal from biomass pyrolysis gas were tested by Phuphuakrat et al. [157] and found that wood chip showed a prominent adsorption selectivity compared with other adsorbents that is suitable for practical use, by minimizing the condensable tar without decreasing the efficiency of the system. In contrast, Chen et al. [158] reported that char type has little effect on tar reduction. Tar emission for rice straw char is slightly smaller than corn straw and fir sawdust char in which the difference of tar emission is within ±1%.

Experimental comparison of commercial biomass chars (C.B. char) with other catalysts (calcined dolomite, olivine, FCC catalyst, biomass ash, and commercial nickel catalyst) for tar reduction was studied by El-Rub et al. [159]. They found that C.B. char gave moderate phenol conversion (82 wt.%) at 700 °C and the highest naphthalene conversion among the low cost catalysts used for tar removal. At 700 °C the ranking of the different catalysts activity for phenol conversion is: nickel > dolomite > FCC > C.B. char > olivine > sand, while the ranking of the different catalysts activity for naphthalene conversion at 900 °C is: nickel > C.B. char > biomass char > biomass ash > FCC > dolomite > olivine > silica sand.

The attractiveness of char as a catalyst originates from its low cost and its natural production inside the gasifier. The disadvantages of char catalyst are coke formation which blocks the pores of char and reduces the surface area of the catalyst, and catalyst loss, as char can be gasified by steam and dry reforming reactions [9].

## 5. Thermal treatment

### 5.1. Thermal cracking

Thermal cracking of tar means that the tar is converted or cracked into lighter gases by heating it at certain temperature for a certain residence time. The high temperature influences the stability of tar converting it into other species. Higher temperature has led to lower yield of tar and higher yields of gaseous products [155,156]. Bridgwater [31] mentioned that biomass-derived tar is very hard to crack by thermal treatment alone. In order to effectively decompose the tar, the following ways were suggested: (1) increasing residence time, such as using a fluidized bed reactor freeboard, but this method is only partially effective; (2) direct contact with an independently heated surface, which required a significant energy supply and decreases the overall efficiency. At the same time, this method is also partly effective and depends on good mixing; and (3) partial oxidation by adding air or oxygen that could increase CO levels at the expense of decrease in conversion efficiency and increase in operational cost.

According to the above paragraph, many studies show that thermal cracking temperature of tar range from 700 to 1250 °C [122,157–159,161–165]. El-Rub et al. [159] reported that thermal conversion of phenol occurs at 700–900 °C. Phenol is stable at a temperature of 700 °C with only 6.3 wt.% conversion, but loses its stability as temperature increases. The conversion is more than 97 wt.% at 800 °C and more than 98 wt.% at 900 °C. In the experiment of Phuphuakrat et al. [157], the reduction of the gravimetric tar mass is 78% in the case of the thermal cracking at 800 °C, whereas, it is in the range of 77–92% in the case of the steam and air forming. Similar results was also described by Chen et al. [158].

It was reported that increasing the temperature and the residence time improve tar cracking, gas production, and char quality (fixed carbon rate more than 90%, volatile matter rate less than 4%) from pyrolysis of pinus pinaster in a two-stage gasifier [166]. Morf et al. [167] found that tar conversion is 88% at isothermal space time 0.12 second and temperature 900 °C from continuous pyrolysis of wood chips. Soot appears to be a major product from homogeneous secondary reactions. In the experiment of Rao and Kunzru [164], the conversion of JP-10 during thermal cracking varies in the range of 10.4–61.1%. The study was done in an annular tubular reactor at atmospheric pressure, in the temperature range of 903–968 K and residence time from 0.7 to 6.4 s. The major products are methane, ethylene, propylene, cyclopentene, cyclopentadiene, benzene and toluene. Fagbemi et al. [165] reported the thermal cracking of tar is effective above 700 °C. From the results, a comparative analysis was done for various biomasses (wood, coconut shell and straw), and a kinetic model of thermal cracking of tar is proposed for a residence time ranging from 0 to 4 s. Sadrameli and Green [168] also did an analytical semi-empirical model (ASEM) of pyrolysis for hydrocarbon thermal cracking. The results suggest that the methodology is useful for identifying pyrolysis yields of other hydrocarbons.

Tar levels and characteristics are also dependent on the feedstock. Myren et al. [122] studied thermal cracking of tar from different raw materials, birch, miscanthus and straw at three different temperatures, 700, 850 and 900 °C. The results are given in Table 11. Main components in the analysed samples are benzene, toluene and naphthalene. Overall, it may be said that the amounts of benzene and naphthalene increase with temperature, while other light tar compounds decrease.

Han and Kim [41] reviewed that to achieve a sufficiently high tar cracking efficiency, the necessary temperature and residence time

**Table 12**
Tar and soot in gas after cracking [41].

| Temperature in reactor (°C) | 1200 | 1250 | 1290 | 1290 |
|---|---|---|---|---|
| Producer gas | Pyrolysis | Pyrolysis | Pyrolysis | Updraft |
| Light tar in condenser determined with GC/MS (mg/kg dry feed stock) | 670 | 21 | 1 | 7 |
| Light tar in aerosol filter determined with GC/MS (mg/kg dry feed stock) | 250 | n.d | 5 | 10 |
| Light tar in soot determined with GC/MS (mg/kg dry feed stock) | n.d | n.d | n.d | 15 |
| PAH in condensate. Sum of 27 components (mg/kg dry feed stock) | 19 | 0.021 | 0.033 | 0.07 |

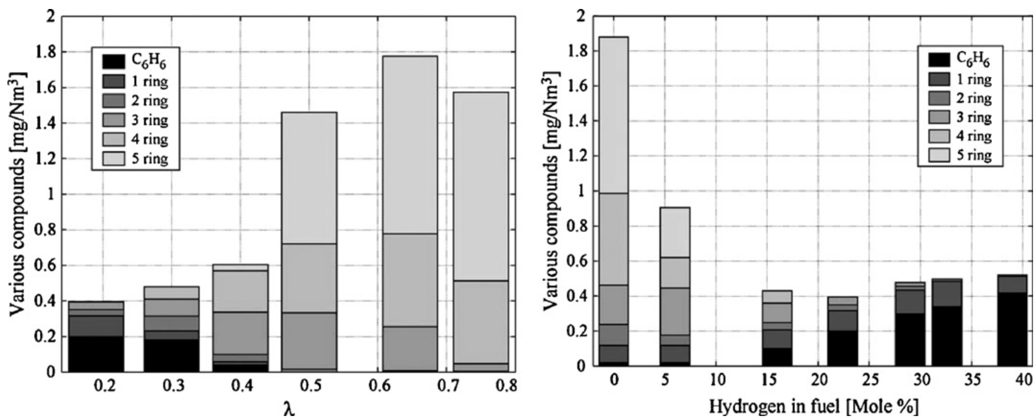



**Fig. 14.** Ring-grouped tar components in the outlet gas as a function of air/fuel ratio (λ) (left) and as a function of hydrogen fraction (right) [170].

were 1250 °C and 0.5 s, respectively. Tar and soot content at 1200, 1250 and 1290 °C are shown in Table 12.

Thermal tar treatment via partial oxidation has been experimentally studied by some researchers [169–172]. Houben et al. [169] carried out tar reduction through partial combustion burner of fuel gas experiment. In this study, naphthalene is added as a model tar component. The effect of partial combustion of the fuel gas mixture on the naphthalene is examined for different air/fuel ratios and varying hydrogen–methane fuel concentrations as shown in Fig. 14. For higher air/fuel ratio values, the total tar content slightly decreases. At lower air/fuel ratio and higher hydrogen concentrations the tar content strongly decreases. It is found that the partial combustion burner reduces the tar content of the gas with over 90% by cracking with an air/fuel ratio of 0.2.

Table 13 shows the distribution of the carbon containing components in the hydrogen–naphthalene–nitrogen flame [169]. Methane, carbon monoxide and carbon dioxide are the components that are most formed in the flame. The gases are formed out of the naphthalene, after most of the oxygen has been consumed. The 2-ring components are really low and even the 3-, 4- and 5-ring components (not shown) are all zero. Clearly, the naphthalene added at the inlet is converted to smaller components in the outlet gas.

**Table 13**
The carbon balance in the no-methane experiment [169].

| | C-input (mg/h) | C-output (mg/h) |
|---|---|---|
| CO | – | 0.4361 |
| $CO_2$ | – | 0.6853 |
| $CH_4$ | – | 0.7164 |
| $C_2H_x$ | – | 0.1246 |
| Benzene ($C_6H_6$) | – | 0.3925 |
| Toluene ($C_7H_8$) | – | 0.0011 |
| Xylene ($C_8H_{10}$) | – | 0.1221 |
| Naphthalene ($C_{10}H_8$) | 2.4919 | 0.0050 |
| Higher-rings | – | – |
| Total | 2.4919 | 2.4919 |

van der Hoeven et al. [170,171] also investigated partial producer gas combustion for tar reduction. The study showed that the influence of ambient gas such as hydrogen on thermal tar conversion can probably be derived from the chemical balance of the reactions taking place. Addition of a certain ambient gas can generate driving forces which can direct or redirect species balance of reactions. The results showed that a rising fuel hydrogen content is always beneficial for increased tar cracking, by increased reaction rates, increased free radical production, and increased radical residence times. Therefore, to obtain best tar cracking by partial product gas combustion, the product gas should have a high fuel hydrogen content. The lower heating value of the product gas rises from 4.1 MJ/N m$^3$ at start-up to approximately 5.3 MJ/N m$^3$ after an hour in operation as shown in Fig. 15.

Partial oxidation (in a mixture stream of oxygen and nitrogen), over a wide temperature range from 600 to 1400 °C was investigated by Zhang et al. [172]. They found that raising the temperature remarkably decreases tar evolution. Benzene and toluene are the most difficult condensable tar species to destroy. The achieve-

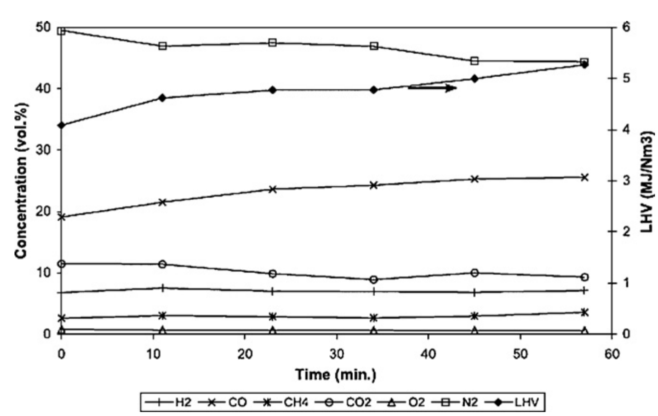



**Fig. 15.** Measured product gas composition after start-up of a 18.5 kW gasification process.

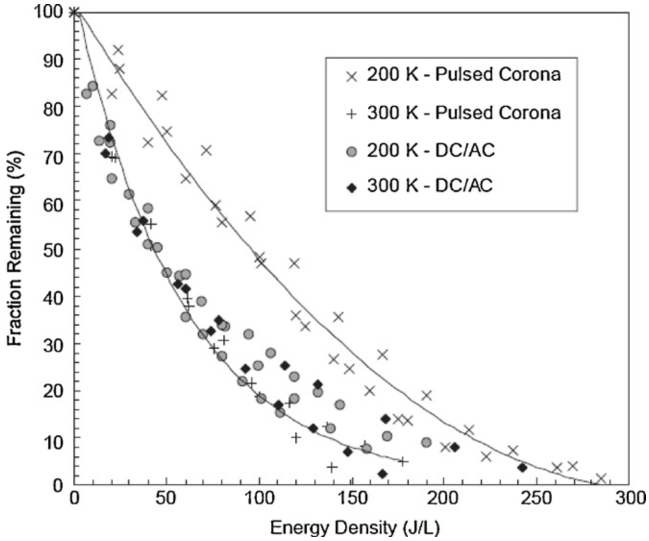



**Fig. 16.** Comparison of the energy consumption for pulsed and DC/AC corona-removal of naphthalene (initial conc. 3–4 g/N $m^3$) from $N_2 + CO_2$ (10%) at various temperatures.

ment of their complete destruction in the producer gas requires extremely high temperatures above 1200 °C, regardless of the gasifying agents. The coke deposits from 900 °C and reaches a maximum formation at 1000 or 1100 °C.

### 5.2. Plasma cracking

Plasma method has been widely investigated for pollution control because of the clean air act. A number of literatures show that plasma method easily removes $CH_4$, $SO_2$ and $NO_x$ from gaseous pollutants [173–183]. Besides, plasma method can also be used as an alternative for catalytic and thermal treatments of tar from producer gas [15,184–188].

Chang [189] reviewed the recent development of integrated electrostatics-plasma pollution control technology to eliminate air pollution. The author mentioned non-thermal plasma reactor should be integrated in a system for effective reductions or oxidations of gaseous pollutants. The available options in non-thermal plasma methods include pulsed corona, dielectric barrier discharges, DC corona discharges, RF plasma, and microwave plasma. Out of these, pulsed corona represents the most feasible method based on chemical efficiency [186].

Nair and co-workers [184–186] used corona plasma system for fuel gas cleaning and found that naphthalene conversion is about 90–95%. They also compared the performance of the pulsed corona to the DC/AC system for naphthalene conversion. Fig. 16 shows the energy density requirements for naphthalene removal under dry reforming conditions at temperatures of 200 and 300 °C, respectively, for both the pulsed corona as well as the DC/AC system. At temperatures of 200 °C, the DC/AC system shows lesser energy requirements as compared to the pulsed corona system. However, at 300 °C, the energy density becomes almost identical.

The application of pulsed corona discharges to crack heavy tar components was also studied by van Heesch et al. [187]. They found that the amount of heavy tar cracking is substantial; 62% is converted at an energy density of 148 J/L, and 68% is converted at an energy density of 161 J/L as shown in Fig. 17. Numerical modeling of naphthalene removal by pulsed corona discharges was also studied [188]. The results showed that the best decomposition has been obtained in pure nitrogen. The reaction of naphthalene with exited nitrogen molecules plays a key role in the cleaning process.

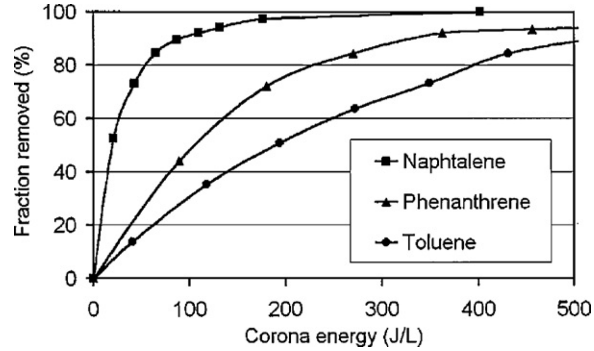



**Fig. 17.** Pulsed corona removal of tar components from dry synthetic biogas in the laboratory setup at 166–194 °C. The gas composition is 17 vol.% $H_2$, 20 vol.% CO, 12 vol.% $CO_2$, 1 vol.% $CH_4$ and balance $N_2$.

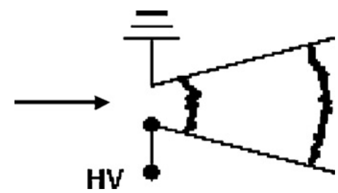



**Fig. 18.** Schematic representation of glid-arc discharge used for tar removal from producer gas.

The use of glid-arc plasma for tar removal was tested at ECN Netherlands [15]. An arc discharge starts at the point where the electrodes are closest. The arc moves along the electrodes, stretching to fill the widening gap, until it breaks and disappears. The discharge creates a plasma of energetic electrons, ions, and radicals that can break down tar compounds in producer gas flowing through the plasma, as indicated in Fig. 18. The results showed that less than 50% of the total tar content was removed at 600 °C, even at plasma energy densities corresponding to 25% of the producer gas energy content. At 800 °C, tar removal was slightly more effective; at 400 °C, it was slightly worse.

Although, these methods are effective for removal of tar from producer gas, they suffer from a number of disadvantages such as limited lifetime of the pulsed power devices, their high costs, and high energy demand of the overall process [189].

## 6. Conclusions

Biomass conversion into producer gas in the gasification process is very useful because it can be used as an alternative fuel to replace the fossil fuels for heat and power generation. The successful application of producer gas depends not only on the quantity of tar, but also on the properties and compositions of tar, which is associated with a dew-point of tar components. In turbines and internal combustion engines using producer gas, tar class 5, 4, and 2 becomes a major cause of condensation which can foul the engines and turbines. Hence, the tar treatment selectivity to remove or convert tar class 5, 4, and 2 is a challenge of future research in producer gas utilization. Mechanical/physical treatments including hot and wet gas cleaning processes can potentially reduce energy conversion efficiency. The novel mechanical treatments such as catalytic filter and OLGA technology are promising to prevent tar deposit in filter and to minimize waste water treatment cost due to the pollution of tar compounds, respectively. Thermal and catalytic conversion methods are more attractive because of the complete destruction of tar. Besides, the methods have higher energy conversion efficiency. However, thermal treatments require supply of energy for the high temperature requirement. Accordingly, there is

a need for economical and optimal method. Basic and acid catalysts although improve the quality of gaseous product, they increase the ash content remaining after char gasification and deactivated rapidly because of coke formation. Char or activated carbon is a cheaper catalyst and naturally produced inside the gasifier, however coke formation blocking the pores is still a problem that must be solved. The use of non-nickel metal catalysts especially rhodium-based catalysts were found as the promising catalyst but they are more expensive than nickel catalysts. Hence, study to extend their lifetime is very necessary to make them more commercially viable. Among all catalysts, nickel catalysts are the most effective to convert tar into fuel gas. Co-impregnation of nickel on natural catalysts (olivine, dolomite, and zeolite) can increase the stability to overcome the carbon deposition, as well as the cost is relatively inexpensive.

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